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Complexes of Cu(II), Ni(II) and Co(II) with isophthalic dihydrazide

C G KUMBHAR

Institute of Armament Technology, Girinagar, Pune 411 025, India

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Abstract. Complexes of isophthalic dihydrazide (IPZ) of the type $MCl_2(IPZ) \cdot H_2O$ [$M = Cu(II), Ni(II), Co(II)$] and $MSO_4(IPZ) \cdot H_2O$ [$M = Cu(II), Ni(II)$] have been prepared and characterised from elemental analysis, magnetic moment, visible, IR, and ESR spectra. Based on these data a polymeric octahedral structure has been assigned to $MCl_2(IPZ) \cdot H_2O$ complexes and sulphate bridged four coordinate polymeric structure for $MSO_4(IPZ) \cdot H_2O$ complexes. Thermogravimetric studies of these complexes show that the thermal stability decreases in the order $Ni(II) > Co(II) > Cu(II)$.

Keywords. Isophthalic dihydrazide ; metal chloride complexes; metal sulphate complexes.

1. Introduction

Benzoyl hydrazide forms complexes with transition (Aggarwal and Narang 1976) and non-transition metals (Aggarwal and Bahadur 1969 ; Aggarwal and Singh 1969) where it is observed that this ligand coordinates through both $>C=O$

$$\begin{array}{c} O \\ || \\ -C \end{array}$$
 and $-NH_2$ of the $-C \begin{array}{c} O \\ || \\ -C \end{array} NH \cdot NH_2$ groups keeping the secondary amino group undisturbed. In metal complexes of $Co(II)$, $Ni(II)$ and $Cu(II)$ with oxalic malonic and terephthalic dihydrazides we have noticed (Kumbhar and Sadasivan 1976)

$$\begin{array}{c} O \\ || \\ -C \end{array}$$
 that these ligands function as bidentate and different $-C \begin{array}{c} O \\ || \\ -C \end{array} NH \cdot NH_2$ groups of the same ligand coordinate to different metal centres resulting in the formation of polymeric complexes. Due to sterically unfavourable positions of hydrazide groups on benzene ring to form chelates when ligand is bifunctional, isophthalic dihydrazide (IPZ) is expected to form polynuclear complexes with metal salts containing both Metal-Nitrogen and Metal-Oxygen bonds simultaneously. In this paper synthesis and characterization of some metal complexes of isophthalic dihydrazide with MCl_2 [$M = Cu(II), Ni(II)$ and $Co(II)$] and MSO_4 [$M = Cu(II)$ and $Ni(II)$] are reported. Thermogravimetric studies of these complexes have also

2. Experimental

Isophthalic acid dihydrazide was synthesised as described in the literature from diethyl isophthalate [M.P. 221° C (Obs), 220° C (Lit)], (Voloviskii and Knoroz 1964). Diethyl isophthalate was prepared after Majumdar and Sharma (1964). Syntheses of metal complexes were carried out by adding hot aqueous solution of ligand to alcoholic solutions of respective metal salts in the molar ratio 1 : 1. Coloured complexes which separated immediately were suction filtered, washed with water, alcohol and ether successively and air-dried.

IR spectra in nujol mull were recorded on Perkin Elmer Spectrophotometer Model 457 using KBr plates. Electronic spectra were obtained in the solid state using nujol mull on Systronics Spectrocolorimeter-103. Magnetic susceptibilities were determined at room temperature by Gouy method using $\text{HgCo}(\text{CN})_5$ as calibrant. ESR spectra were recorded on Varian Microwave Spectrometer in the x-band region (9.1 GHz) using DPPH as internal standard. Thermogravimetric study was carried out using MOM-BUDAPEST Model by heating samples at a rate of 10° C per minute.

3. Results and discussions

3.1. Physical properties of complexes

The elemental analysis and physical properties of the complexes are listed in table 1. The complexes are quite stable in air. They are insoluble in common organic solvents and water. However, they decompose in mineral acids and are sparingly soluble in DMF and pyridine. Molecular weights of these complexes could not be measured as they are insoluble in suitable solvents. Elemental analysis leads to the stoichiometry $\text{MCl}_2(\text{IPZ}) \cdot \text{H}_2\text{O}$ [M = Cu(II), Ni(II) and Co(II)] and $\text{MSO}_4(\text{IPZ}) \cdot \text{H}_2\text{O}$ [M = Cu(II) and Ni(II)] for the complexes. The association of one water molecule is confirmed both from IR spectra and thermogravimetric data.

Table 1. Analytical data and physical properties of the complexes.

Sl. No.	Compound	Colour	% M		% Cl/S		$\mu_{\text{eff.}}$ BM	g values
			Found	Cal.	Found	Cal.		
1.	$\text{CuCl}_2(\text{IPZ}) \cdot \text{H}_2\text{O}$	Green	18.00	18.34	19.90	20.46	2.00	2.19
2.	$\text{NiCl}_2(\text{IPZ}) \cdot \text{H}_2\text{O}$	Light blue	16.90	17.20	21.00	20.76	2.82	2.18
3.	$\text{CoCl}_2(\text{IPZ}) \cdot \text{H}_2\text{O}$	Pink	16.90	17.24	19.90	20.73	4.42	..
4.	$\text{CuSO}_4(\text{IPZ}) \cdot \text{H}_2\text{O}$	Blue	17.00	17.10	8.20	8.61	1.74	2.16
5.	$\text{NiSO}_4(\text{IPZ}) \cdot \text{H}_2\text{O}$	Light blue	15.90	16.01	8.22	8.53	2.98	2.18

valent to one water molecule is also evident in the TG and DTA curves at $\approx 110^\circ\text{C}$. Thus the presence of free water molecule is indicated. Coordinated water would have lost at relatively higher temperatures. The $\nu\text{-N-H}$ frequencies are lower by $50\text{--}100\text{ cm}^{-1}$ as compared to their respective positions in the parent ligand. The $\nu\text{-C=O}$ is also shifted to lower region in the complexes by $35\text{--}40\text{ cm}^{-1}$. The shift to lower wave numbers of the amino and carbonyl vibration bands in all the complexes is a clear indication of the involvement of both -NH_2 and >C=O in coordination. The possibility of enol form is not indicated in the IR spectra of the complexes. The new strong band appearing in the region $1200\text{--}1230\text{ cm}^{-1}$ has been assigned to $\nu\text{-(C-O)}$ (Aggarwal *et al* 1976). The medium to weak band in the region $550\text{--}600\text{ cm}^{-1}$ is assigned to $\nu\text{-M-O}$ following Adams (1967) who has shown that $\nu\text{-M-O}$ stretching frequency in the metal carbonyl complexes occurs around 600 cm^{-1} . It is observed that $\nu\text{-M-O}$ is higher for MSO_4 complexes than for MCl_2 complexes.

Electronic spectra of MCl_2 complexes give evidence for distorted octahedral symmetry around metal centre. Thus CuCl_2 complex shows broad bands around 640 nm and 560 nm which are characteristic bands for octahedral environment around Cu(II) (Billing and Underhill 1968; Mahapatra and Rama Rao 1971). Ni(II) complex shows broad bands at 660 nm and 580 nm and weak bands at 520 nm and 490 nm . Manch and Fernelius (1961) have also observed such bands for octahedral Ni(II) in the region $700\text{--}350\text{ nm}$. CoCl_2 complex shows broad bands at 650 nm , 625 nm and 505 nm which are characteristic bands for octahedral environment around Co(II) ion (Aggarwal *et al* 1976). Magnetic moment values (table 1) of the complexes of CuCl_2 (2.00 B.M.), NiCl_2 (2.82 B.M.) and CoCl_2 (4.42 B.M.) show one, two and three unpaired electrons respectively and are well within the range required for octahedral environment around metal centre (Figgis and Lewis 1960).

The average 'g' value for CuCl_2 complex ($g = 2.19$) calculated from ESR spectra of polycrystalline powder samples is comparable to those reported for Cu(II) complexes with octahedral symmetry (Sadasivan and Arora 1976). Similarly 'g' value for NiCl_2 complex ($g = 2.18$) is also consistent with those observed for Ni(II) complexes having octahedral symmetry (Arora and Kumbhar 1977).

Thus in the $\text{MCl}_2 \cdot \text{L} \cdot \text{H}_2\text{O}$ complexes the stoichiometry and bidentate nature of ligand suggest a polymeric structure as shown in figure 1a. The stoichiometry and insolubility of the compounds in common organic solvents support this contention.

Although electronic spectra for $\text{CuSO}_4(\text{IPZ}) \cdot \text{H}_2\text{O}$ complex exhibit broad band at 550 nm consistent with tetragonally distorted octahedral structure, the effective magnetic moment (1.74 B.M.) value is comparable to the values reported for square planar and tetrahedral copper sulphate complexes (Saconi and Ciapolini 1964; Beadle *et al* 1969). The tetrahedral Cu(II) complexes have the magnetic moment values within the range $1.89\text{--}1.92\text{ B.M.}$ and square planar Cu(II) in the range $1.83\text{--}1.86$ (Saconi 1966). The observed magnetic moment value for $\text{CuSO}_4(\text{IPZ}) \cdot \text{H}_2\text{O}$ is more close to square planar symmetry. The splitting of the strong

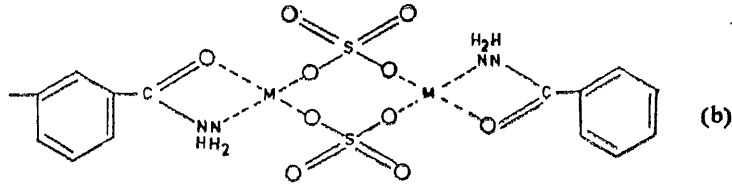
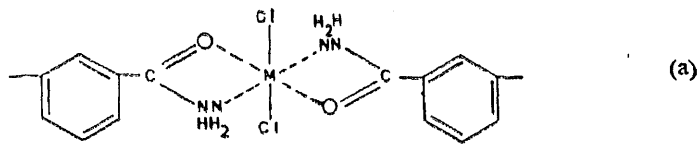


Figure 1. (a) Proposed structure for MCl_2 complexes [$M = Cu(II), Ni(II), Co(II)$].
(b) Proposed structure for $[MSO_4]$ complexes $M = Cu(II), Ni(II)$.

sulphate bands in the infrared spectrum (bands at 1175 cm^{-1} , 1130 cm^{-1} , 1050 cm^{-1}) is consistent with bidentate bridged SO_4^{2-} ion (Nakamoto *et al* 1957). Hence square planar polymeric structure is suggested for $CuSO_4(IPZ) \cdot H_2O$ consisting of bidentate ligand and bridging sulphate ion as shown in figure 1b.

$NiSO_4 \cdot L \cdot H_2O$ shows broad band at 580 nm which is characteristic for tetrahedral nickel complexes (Saconi 1966). Literature survey reveals (Yamada 1966) that square planar nickel complexes are diamagnetic and red in solid state. Magnetic moment value for $NiSO_4$ complex (2.98 B.M.) is within the range for tetrahedral environment. The possibility of pseudo-tetrahedral environment is rather less because such complexes possess magnetic moment in the range $3.2\text{--}3.3\text{ B.M.}$ (Saconi 1966). Hence we are tempted to suggest a tetrahedral polymeric structure for $NiSO_4(IPZ) \cdot H_2O$ (figure 1b).

3.3. Thermogravimetric analysis

Thermogravimetric study of all the complexes show almost similar decomposition pattern. The DTA peaks are given in table 2. The endothermic peaks at $105\text{--}110^\circ\text{C}$ in all the complexes on DTA curve is accompanied by weight loss equivalent to one water molecule on TG curve.

In the case of MCl_2 complexes loss of chlorine occurs in the temperature range $105\text{--}320^\circ\text{C}$ which is followed by elimination of amine groups in the temperature range $300\text{--}450^\circ\text{C}$, with subsequent decomposition of the ligand and carbonization of the aromatic ring residue which spreads over the temperature range $450\text{--}600^\circ\text{C}$. The formation of respective metal oxides occurs at $600\text{--}700^\circ\text{C}$. The thermogravimetric

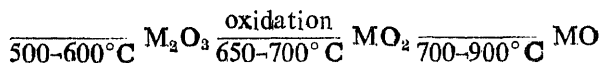
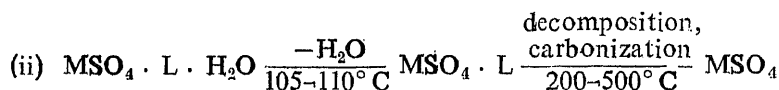
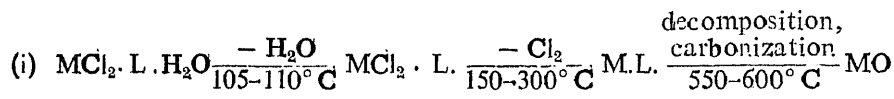
Table 2. Thermal decomposition data. MCl_4 and MSO_4 complexes.

Compound	DTA peak temp. ($^{\circ}C$)				
$CuCl_2(IPZ) \cdot H_2O$	110 (-)	215 (+)	360 (+)		
$NiCl_2(IPZ) \cdot H_2O$	105 (-)	330 (+)	425 (+)		
$CoCl_2(IPZ) \cdot H_2O$	100 (-)	250 (+)	450 (+)	600 (+)	640 (+)
$CuSO_4(IPZ) \cdot H_2O$	110 (-)	240 (+)	420 (+)	720 (-)	
$NiSO_4(IPZ) \cdot H_2O$	105 (-)	280 (+)	340 (+)	440 (+)	530 (+)
		750 (-)			

(-) and (+) signs after temperatures represent endotherm and exotherm respectively.

For MSO_4 complexes, after the elimination of one water molecule and decomposition of amino groups, formation of anhydrous MSO_4 takes place at temperature around $500^{\circ}C$. Anhydrous MSO_4 finally decomposes to respective metal oxide *via* intermediate oxide formation as represented below. Formation of MO to MO_2 is evidenced by peaks at 720 and $750^{\circ}C$ on DTA curves for Cu(II) and Ni(II) complexes, which are also supported by the corresponding peaks on DTA curves at the same temperature. Percentage residue observed on TG curve also agrees well with calculated values for each intermediate stage of decomposition.

The decomposition pattern for MCl_2 and MSO_4 complexes can be represented as



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Amorphous MoS_3 and A_xMoS_3 ($\text{A} = \text{Li}$ or Na ; $0 < x < 4$)†

T MURUGESAN and J GOPALAKRISHNAN*

Solid State and Structural Chemistry Unit, Indian Institute of Science,
Bangalore 560 012, India

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Abstract. Amorphous A_xMoS_3 ($\text{A} = \text{Li}$ or Na ; $0 < x < 4$) prepared by the reaction of MoS_3 with *n*-butyllithium or sodium naphthalide in organic solvents have been characterized by x-ray photoelectron spectroscopy, infrared spectroscopy as well as electrical and magnetic measurements. The results indicate that sulphur exists as polysulphide species in MoS_3 and mainly as monosulphide in A_xMoS_3 when $x \sim 4$; there is no discernible change in the $\text{Mo}(3d)$ binding energies of MoS_3 and A_xMoS_3 . Both MoS_3 and A_xMoS_3 are diamagnetic and non-metallic at room temperature. The data suggest that MoS_3 probably exists as $\text{Mo}^{3+}(\text{S}_3^{2-})$ with Mo-Mo bonds, incorporation of alkali metal atoms resulting in the reduction of proportion of polysulphide ions.

Keywords. Amorphous MoS_3 ; Li_xMoS_3 ; Na_xMoS_3 ; x-ray photoelectron spectra.

1. Introduction

Among the transition metal trisulphides MS_3 ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}, \text{Nb}, \text{Ta}, \text{Mo}$ and W), MoS_3 and WS_3 can be prepared only in the amorphous state by low-temperature chemical or thermal decomposition of ammonium tetrathiometalates (Wildervanck and Jellinek 1964; Diemann 1977). Until recently, the identity of these sulphides as true chemical compounds was somewhat in doubt. It has now been established that these are definite compounds (not a mixture of disulphide and amorphous sulphur) possessing a chain-like structure similar to that of crystalline trichalcogenides of other transition metals (Liang *et al* 1980a,b). It has recently been found that MoS_3 can incorporate reversibly upto four atoms of alkali metal per formula unit, A_xMoS_3 ($\text{A} = \text{alkali metal}$; $0 < x < 4$) making it a good candidate for cathode material in solid state batteries (Jacobson *et al* 1979). A_xMoS_3 may be regarded as thioanalogues of the alkali metal oxygen bronzes of molybdenum. We have investigated the structure and electronic properties of MoS_3 and A_xMoS_3 ($\text{A} = \text{Li}$ or Na) by various physical methods in an attempt to understand the nature of these solids.

† Contribution No. 125 from the Solid State and Structural Chemistry Unit.

* To whom all correspondence should be made.

2. Experimental

MoS_3 was prepared by thermal decomposition of $(\text{NH}_4)_2\text{MoS}_4$ at 500 K in stream of dry nitrogen (Jacobson *et al* 1979). The composition was found to be $\text{MoS}_{2.98}$ from the chemical analysis of sulphur [S (found) = 49.73% ; S (calc.) = 50.06%]. Samples of Li_xMoS_3 ($x = 0.9, 2.2$ and 3.7) and Na_xMoS_3 ($x = 0.8$ and 3.5) were prepared, as reported in the literature (Jacobson *et al* 1979), by reaction with *n*-butyllithium in *n*-hexane and sodium naphthalide in tetrahydrofuran respectively. To prepare Li_xMoS_3 , a known amount of MoS_3 was treated with a 1 M solution of *n*-butyllithium in *n*-hexane in a flowing nitrogen atmosphere. After the reaction, the solid was filtered and the concentration of *n*-butyllithium in the filtrate was determined by the addition of standard potassium hydrogen phthalate and back titration with standard potassium hydroxide. From the difference in concentration, the amount of lithium inserted into MoS_3 was calculated. Similarly samples of Na_xMoS_3 were prepared by reaction of MoS_3 with sodium naphthalide in dry tetrahydrofuran followed by determination of the concentration of sodium naphthalide in the filtrate as in the case of reaction with *n*-butyllithium. Details are given in table 1.

X-ray powder diffraction patterns, recorded with CuK_α radiation, showed broad diffuse scattering with a maximum around $14^\circ 2\theta$. The diffuse band became sharper with increasing alkali metal content in A_xMoS_3 . The absence of any other discrete diffraction lines in the patterns indicates that the samples are x-ray amorphous similar to MoS_3 .

X-ray photoelectron spectra (XPS) of the samples were recorded with a ESCA-Mark II sepectrometer (VG Scientific Co. Ltd., UK) using AlK_α radiation. Infrared spectra were recorded with a Perkin-Elmer Model 580 spectrometer. Electrical resistivities of the pelletized samples were measured by a two-probe technique. Magnetic susceptibilities were measured by Faraday method between 150–300 K.

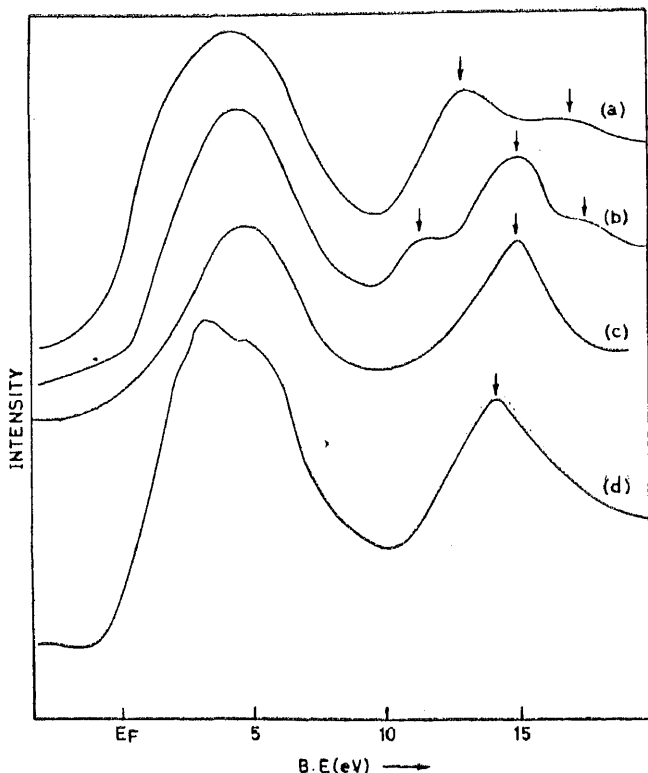
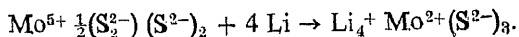
Table 1. Preparation of A_xMoS_3 ($\text{A} = \text{Li}$ or Na ; $0 < x < 4$).

Amount of MoS_3 , g (m moles)	Concentration of <i>n</i> -butyllithium or sodium naphthalide (m moles)		Alkali metal inserted per mole of MoS_3 (moles)	Composition
	Before the reaction	After the reaction		
2.88 (15)	13.50	0.0	0.9	$\text{Li}_{0.9}\text{MoS}_3$
2.88 (15)	33.00	0.0	2.2	$\text{Li}_{2.2}\text{MoS}_3$
2.40 (12.5)	50.00	3.75	3.7	$\text{Li}_{3.7}\text{MoS}_3$
3.84 (20)	16.00	0.0	0.8	$\text{Na}_{0.8}\text{MoS}_3$

3. Results and discussion

We have studied the valence band and core level XPS of MoS_3 , $\text{Li}_{0.9}\text{MoS}_3$, $\text{Li}_{2.2}\text{MoS}_3$ and $\text{Li}_{3.7}\text{MoS}_3$ to find out the nature of molybdenum and sulphur in these compounds. The spectra are given in figures 1 and 2 and the binding energies in table 2. For purpose of comparison, the spectra of MoS_2 are also included in the figures.

The $\text{S}(3s)$ peak of MoS_3 occurs as a doublet at 12.7 and 16.6 eV binding energies in contrast to a single (3s) peak at 14 eV in the case of MoS_2 (figure 1). To account for the doublet structure, it was proposed in our earlier study from this laboratory (Manthiram *et al* 1980) that two different kinds of sulphur are present in MoS_3 : $\text{Mo}^{4+}(\text{S}_2^{2-})(\text{S}^{2-})$. Similar $\text{S}(3s)$ doublet structure in MoS_3 with a relative intensity of 2 : 1 has been found by Liang *et al* (1980a). They proposed that MoS_3 consists of $\frac{1}{2}\text{S}_2^{2-}$ and 2S^{2-} which requires that molybdenum is present in 5+ formal oxidation state : $\text{Mo}^{5+}\frac{1}{2}(\text{S}_2^{2-})(\text{S}^{2-})_2$. According to this formulation, formation of A_xMoS_3 with x upto four would imply a reduction of Mo^{5+} to Mo^{2+} :



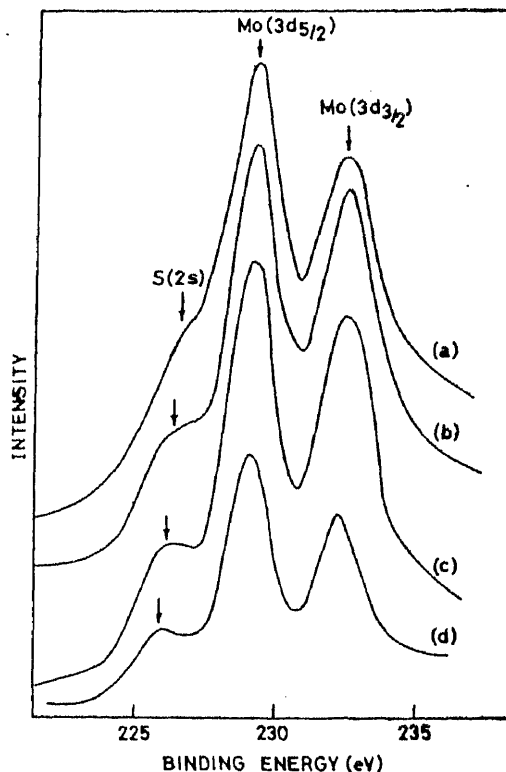


Figure 2. S(3s) and Mo(3d_{5/2}, 3d_{3/2}) core level spectra of (a) MoS₃, (b) Li_{0.9}MoS₃, (c) Li_{1.2}MoS₃ and (d) MoS₃.

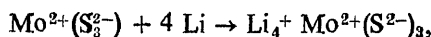
Table 2. XPS binding energy, electrical resistivity and magnetic susceptibility data of MoS₃ and A_xMoS₃ (A = Li or Na; 0 < x < 4).

Compound	S(3s) binding energy (eV)	S(2s) binding energy (eV)	Mo(3d _{5/2}) binding energy (eV)	Electrical resistivity ρ at 300 K (Ohm-cm)	Magnetic susceptibility $\chi_m \times 10^6$ at 300 K (cgs emu)
MoS ₃	12.7, 16.6	226.7	229.1	3.8×10^4	-48
Li _{0.9} MoS ₃	11.2, 14.8, 17.3	226.4	229.1	4.6×10^4	-67
Li _{1.2} MoS ₃	broad	226.4	229.1	3.6×10^4	-86
Li _{3.7} MoS ₃	14.8	226.3	229.1	4.0×10^4	-92
Na _{0.9} MoS ₃	11.2, 14.8, 17.3	226.4	229.1	3.4×10^4	-70

in $\text{Li}_{0.9}\text{MoS}_3$ and $\text{Li}_{2.2}\text{MoS}_3$, the $\text{S}(3s)$ shows complex features and at the limiting composition $\text{Li}_{3.7}\text{MoS}_3$, the $\text{S}(3s)$ becomes a single band similar to that in MoS_2 . In addition, the $\text{Mo}(3d)$ binding energies remain almost constant [229.1 eV for $\text{Mo}(3d_{5/2})$] in MoS_3 and Li_xMoS_3 . We also see a slight decrease in the $\text{S}(2s)$ binding energy as we go from MoS_3 to $\text{Li}_{3.7}\text{MoS}_3$ (table 2). The results seem to indicate that incorporation of alkali metal into MoS_3 affects only sulphur and not molybdenum.

If we assume that MoS_3 consists of a trisulphide ion, S_3^{2-} , and Mo-Mo chain, $\text{Mo}^{2+}(\text{S}_3^{2-})$, the experimental results can be explained as follows :

(i) incorporation upto a maximum of four alkali metal atoms without change in the oxidation state of molybdenum,



(ii) presence of two different kinds of sulphur in MoS_3 in the ratio 2 : 1, and

(iii) the complex nature of $\text{S}(3s)$ at intermediate values of x in A_xMoS_3 . In these cases, the polysulphide ion bonds would have been partially broken resulting in S_3^{2-} , and S_2^{2-} species.

Infrared absorption spectra and electrical and magnetic properties of A_xMoS_3 are consistent with the above model. MoS_3 shows characteristic S-S stretching vibration of the polysulphide ion at 515 and 540 cm^{-1} as shown in figure 3 (Rittner *et al* 1979). The disappearance of these bands in $\text{Li}_{3.7}\text{MoS}_3$ indicates that polysulphide species is absent. In addition, a new band at 420 cm^{-1} appears in Li_xMoS_3 ; the band may be assigned to Li-S stretching vibration. Similar changes in the infrared spectra of Li_xTiS_3 have been reported by Chianelli and Dines (1975).

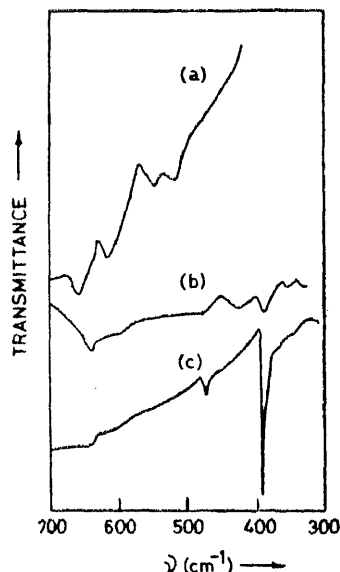


Figure 3. Infrared spectra of (a) MoS_3 , (b) $\text{Li}_{3.7}\text{MoS}_3$ and (c) MoS_3 (crystalline)

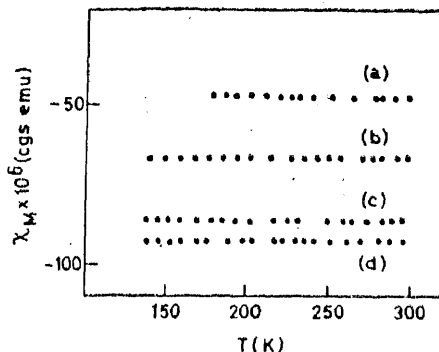
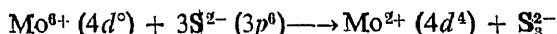


Figure 4. χ_M - T plots for (a) MoS_3 , (b) $\text{Li}_{0.9}\text{MoS}_3$, (c) $\text{Li}_{2.2}\text{MoS}_3$ and (d) $\text{Li}_{2.7}\text{MoS}_3$.

Room temperature electrical resistivity, ρ , and magnetic susceptibility, χ_M , of MoS_3 and A_xMoS_3 are given in table 2. It is seen that there is no significant difference between the resistivities of MoS_3 and A_xMoS_3 . The magnetic susceptibility data (figure 4) show that the diamagnetic character of MoS_3 is retained in A_xMoS_3 albeit with increase in the magnitude of diamagnetic χ_M . The results support our formulation of MoS_3 as $\text{Mo}^{2+}(\text{S}_3^{2-})$, the diamagnetism being due to Mo-Mo bonds as proposed by Liang *et al* (1980a). Insertion of alkali metal does not seem to disrupt the Mo-Mo bonds in MoS_3 .

The presence of molybdenum in a formal oxidation state of 2+ in MoS_3 can be understood in terms of Jellinek's (1968) model for transition metal sulphides. Transition metal ions having large positive oxidation state such as Mo^{6+} and W^{6+} would be unstable in the solid state in the presence of S^{2-} ions because the valence $\text{S}(3p)$ states overlap with the empty $\text{Mo}(4d)$ or $\text{W}(5d)$ states, resulting in electron transfer from $\text{S}(3p)$ to the $\text{M}(d)$ until the metal d -states are lifted just above those of $\text{S}(3p)$. In chemical terms, this would correspond to the reduction of the metal ion to lower oxidation states and oxidation of sulphide to polysulphide :



A formal oxidation state around 2+ for molybdenum as well as Mo-Mo bonds occur in molybdenum sulphides, e.g. Chevrel phases, $\text{A}_x\text{Mo}_6\text{S}_8$ (Yvon 1978).

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Synthesis of 1,5-disubstituted-2,4-dithiobiuret and 1,5-disubstituted-2-thiobiuret and their vanadyl (V) chloride complexes

K. P. SRIVASTAVA and I. K. JAIN*

Chemistry Group, Birla Institute of Technology and Science, Pilani 333 031, India

* Present address : Geological Survey of India, Bhopal 462 002, India

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Abstract. Vanadyl (V) chloride forms $\text{VOCl}_3 \cdot \text{L}$ (L is a bidentate ligand molecule) type complexes with 1,5-disubstituted 2,4-dithiobiurets and 1,5-disubstituted-2-thiobiurets in carbon tetrachloride solution. Co-ordinations through sulphur atoms in case of 1,5-diaryl substituted 2,4-dithiobiurets and sulphur and oxygen in case of 1,5-diaryl substituted 2-thiobiurets have been proposed for these complexes.

Keywords. Vanadyl (V) chloride complexes ; 1,5-disubstituted 2,4-dithiobiurets ; 1,5-disubstituted-2-thiobiurets.

1. Introduction

Vanadyl(V) chloride forms $\text{VO}(\text{NHPh})_3$ type complex (Nelson and McFadden 1933) with aniline. Addition and substitution complexes of VOCl_3 are also known (Bunk *et al* 1958 ; Krauss and Gnatz 1962 ; Cozzi and Cecconi, 1953). Reduction of VOCl_3 by carboxylic acids, pyridine and aliphatic amines and thioethers with the formation of vanadyl (IV) carboxylates, $\text{VOCl}_2 \cdot 3 \text{C}_6\text{H}_5\text{N}$ and $\text{VOCl}_2 \cdot 2\text{L}$ where L is CH_3NH_2 ; $(\text{CH}_3)_2\text{S}$ and $(\text{C}_2\text{H}_5)_2\text{S}$ respectively is also reported (Selbin 1953 ; Paul and Kumar 1965 ; Baker *et al* 1967). Some unreduced $\text{VOCl}_3 \cdot 2\text{L}$ type VOCl_3 complexes with aromatic amines are also said to have been synthesized (Prasad and Upadhyaya 1960).

From the literature it has been found that no work has been carried out on complexing ability of VOCl_3 with polydentate ligands. We have synthesized the 1,5 disubstituted-2,4-dithiobiurets and 1,5-disubstituted-2-thiobiurets ligands and their VOCl_3 complexes.

2. Experimental

All the chemicals used were of either BDH "AnalaR" or MERCK GR grade. Solvents were purified by repeated distillation after appropriate drying. Phenyl isocyanate (mustard oil) used was of E. MERCK. Other mustard oils viz, phenyl, ortho-tolyl and para-tolyl isothiocyanate were prepared in the laboratory

* To whom all correspondence should be made.

gel 1962). Vanadyl (V) chloride was prepared (Hecht *et al* 1947 ; Prandtl Bleyer 1909) by refluxing and distilling the mixture of V_2O_5 and $SOCl_2$. It analysed to check its purity. Data are reported in table 1.

Synthesis of substituted dithiobiurets and thiobiurets ligands

ligands 1,5-diphenyl 2,4-dithiobiuret (DPDTB) ; 1,5-diphenyl 2-thiobiuret (TB) ; 1-phenyl 5-paratolyl 2,4-dithiobiuret (P.*p*-TDTB) ; 1-phenyl 5-para-2-thiobiuret (P.*p* TTB) ; 1-orthotolyl-5-phenyl 2,4-dithiobiuret (*o*-TPDTB ; orthotolyl-5-phenyl-2-thiobiuret (*o*-TPTB) ; 1,5-diparatolyl 2,4-dithiobiuret (DTPDTB) ; 1,5-diorthotolyl 2,4-dithiobiuret (D-*o*-TDTB) and 1-methyl-5-orthotolyl 2,4-dithiobiuret (Me-*p*-TDTB) were prepared by the known method (Prandtl 1962). Purity of ligands was checked by their sharp melting points and elemental analysis (table 1).

Preparation of complexes

Reactions were carried out in a dry box. The ligand was dissolved in minimum of chloroform and then 0.02 M solution was prepared by CCl_4 . $VOCl_3$ solution in CCl_4 (0.03 M) was added to the ice-cold ligand solution. The temperature of reaction mixture was kept below $10^\circ C$. The coloured complex was isolated, washed, dried and then analysed for vanadium, chloride and sulphur (Prandtl 1959).

Instrumentation

Magnetic measurements of the complexes were carried out on Gouy balance. Molar conductance was determined in N,N-dimethyl formamide (10^{-3} M) on conductivity meter type LBR of Wissenschaftlich Technisch, Wersstatten, Germany, using a dip type cell. The IR spectras were taken on Perkins Elmer Grating infra-red spectrophotometer model 237-B and 621. The important peaks of spectra are listed in table 2.

Results and discussion

Analytical results (table 1) correspond to the empirical formula $VOCl_3 \cdot L$, where L is a ligand molecule. The molar conductance values are in the range of 32.96-55.5 Mhos which are well below those for 1 : 1 electrolyte (Suttons 1971). The observed conductance values seem to be due to the partial replacement of chloroform by solvent molecule. All the complexes are diamagnetic with a magnetic susceptibility $(-0.19 \text{ to } -0.43) \times 10^{-6}$. The presence of the ligands a medium broad band appearing around 3100-3200 may be due

Table 1. Colour, melting point and analytical data.

Substance	M.pt. °C	Colour	% found			% calculated		
			V	S	Cl	V	S	C
VOCl ₃	..	Reddish yellow	29.46	..	62.10	29.39	..	61
DPDTB	144	White	..	21.83	..	..	22.28	22
VOCl ₃ .DPDTB	96	Blackish green	10.93	13.21	22.01	11.06	13.89	22
DPTB	158	White	..	10.94	..	..	11.80	22
VOCl ₃ .DPTB	99	Light green	11.94	6.94	24.12	11.46	7.20	22
P- <i>p</i> -TDTB	123	Yellowish white	..	23.00	..	..	21.25	22
VOCl ₃ .P- <i>p</i> -TDTB	97	Green	11.14	13.02	23.12	10.73	13.48	22
P- <i>p</i> -TTB	189	Light yellow	..	11.53	..	..	11.22	22
VOCl ₃ .P- <i>p</i> -TTB	103	Bluish green	12.04	7.12	24.10	11.11	6.98	22
<i>o</i> -T.PDTB	118	Light yellow	..	22.01	..	..	21.25	22
VOCl ₃ . <i>o</i> -TPDTB	98	Yellowish green	10.93	13.58	23.02	10.73	13.48	22
<i>o</i> -T.PTB	174	Light green		10.94	..	..	11.22	22
VOCl ₃ . <i>o</i> -T.PTB	101	Light yellow	10.81	7.41	22.70	11.11	6.98	22
D- <i>p</i> -TDTB	142	White	..	21.46	..	..	20.30	21
VOCl ₃ .D- <i>p</i> -TDTB	93	Light yellow	9.84	14.02	22.10	10.43	13.10	21
D- <i>o</i> -IDTB	126	Yellowish white	..	21.14	..	..	20.30	21
VOCl ₃ .D- <i>o</i> -IDTB	94	Green	11.12	12.83	20.93	10.43	13.10	21
Me- <i>p</i> -IDTB	152	Light yellow	..	27.12	..	..	26.76	22
VOCl ₃ .Me- <i>p</i> -IDTB	103	Bluish green	13.01	16.12	27.01	12.35	15.51	22

Table 2. IR spectral data and tentative assignments (cm⁻¹).

Compound	(-NH) stretch	(C=O) stretch	(N-H) deformation	(C=S) stretch	Phenyl ring + (CN) stretch	(CS + CN) stretch	(NH) rock- ing + $\nu(\text{N}-\text{C}-\text{N})$ + $\nu(\text{C}=\text{S})$	(N=O) stretch
DTB	3120 m	..	1615 m	750 s	1535 s	1250 s	1480 m	..
3 ₃ (DPDTB)	3125 m	..	1610 m	740 m	1550 b	1240 m	1470 vw	1020 m
3 ₃	3230 s	1710 s	1600 vs	790 m	1500 vs	1227 s	1435 m	..
3 ₃ (DPFB)	3220 mb	1700 m	1595 m	765 m	1510 m	1220 s	1430 m	1030 m
TDTB	3250 s	..	1600 s	750 w	1540 s	1260 mb	1465 m	..
3 ₃ (P-p-TDTB)	3255 m	..	1605 m	740 m	1540 m	1245 m	1455 s	1025 mb
TTTB	3196 w	1715 s	1620 s	785 w	1525 s	1295 m	1460 m	..
3 ₃ (P-p-TTB)	3200 mb	1710 m	1625 s	765 mb	1530 m	1285 mb	1450 s	1030 m
PDTB	3235 m	..	1615 m	755 s	1570 m	1245 sb	1450 b	..
3 ₃ (o-T-PDTB)	3230 mb	..	1635 m	740 mb	1575 w	1225 mb	1445 m	995 m
PTB	3250 vs	1715 s	1620 vs	755 m	1540 m	1245 sb	1450 s	..
3 ₃ (o-T-PTB)	3260 s	1695sb	1620 m	740 mb	1515 mb	1230 mb	1480 sb	975 m
3 ₃ -TDTB	3160 m	..	1625 m	795 s	1515 b	1155 m	1455 s	..
3 ₃ (D-p-TDTB)	3150 m	..	1620 sw	740 wb	1510 w	1165 s	1440 mb	980 w
3 ₃ -TDTB	3215 m	..	162 s	750 s	1560 s	1260 m	1502 s	..
3 ₃ (D.o-TDTB)	3210 mb	..	1635 s	740 s	1575 m	1245 s	1490 m	940 s
3 ₃ -TDTB	3230 m	..	1610 m	755 m	1555 s	1255 m	1500 m	..
3 ₃ (Me-p-TDTB)	3240 mb	..	1620 s	730 mb	1600 s	1205 wb	1480 s	1005 m

s = strong, w = weak, vw = very weak, m = medium, b = broad.

et al 1967 ; Yamaguchi *et al* 1958). Both these bands on complexation are shifted down by $10\text{--}20\text{ cm}^{-1}$ with reduced intensity which indicates the possibility of thioketo sulphur atoms as co-ordination sites in complexes. The bands $\sim 1450\text{ cm}^{-1}$ in ligands are assigned to the NH-C=S group vibration which is the combination of $\nu(\text{N-C-N})$, $\nu(\text{C=S})$ and -NH rocking vibrations (Yamaguchi *et al* 1958 ; Randall 1949). The change in the nature of these vibrations on complexation further confirms the ligand co-ordination to the metal atom through thioketo sulphur atoms.

In DPTB, *P.p*-TTB and *o*-TPTB ligands, the sharp peaks appearing around 1710 cm^{-1} have been assigned to the vibrations of $\nu(\text{C=O})$ group (Srivastava and Madhok 1978). On complexation the $\nu(\text{C=O})$ absorption peak shifts to a lower frequency by $10\text{--}20\text{ cm}^{-1}$ and becomes medium in intensity. The V=O stretching vibrations in the complexes appear $\sim 1030\text{ cm}^{-1}$. These bands are weak and medium in intensity and are in the region expected for vanadium oxygen stretching frequencies (Miller and Cousins 1957).

All these observations show that co-ordination of DPDTB, *P.p*-TDTB, *o*-TPDTB, *D.p*-TDTB, *D.o*-TDTB and *Me.p*-TDTB ligands to the metal atom is through two thioketo sulphur atoms while in the case of DPTB, *P.p*-TTB and *o*-TPTB ligands it is through thio-keto sulphur and C=O group oxygen atoms. The six coordinated complexes $[\text{VOCl}_3(\text{L})]$ so formed may have octahedral configuration.

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Precipitation of uranium quinolin-8-olate from homogeneous solution by urea hydrolysis

G SIVA REDDY†, A VARADA REDDY and
Y KRISHNA REDDY*

Department of Chemistry, SV University, Tirupati 517 502, India

† Present address : SVUPG Extension Centre, Cuddapah, India

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Abstract. A very crystalline precipitate of uranium quinolin-8-olate (uranyl oxinate) has been obtained from homogeneous solution by utilising urea hydrolysis to raise the pH of the initially acid solution of uranium (VI) in the presence of sodium acetate and the precipitant. The precipitate so obtained is stoichiometric unlike the one obtained in conventional precipitation and possesses the same composition (uranium : oxine ratio) irrespective of the pH of the final solution unlike that obtained in earlier PFHS methods. The results obtained show that the determination is not affected by the presence of other metal ions when the precipitation is carried out in the presence of EDTA and the precipitate obtained by PFHS is also more thermally stable.

Keywords. Uranium(VI) complex ; quinolin-8-ol ; precipitation from homogeneous solutions ; urea hydrolysis ; thermal analysis.

1. Introduction

Precipitation from homogeneous solution (PFHS) technique is often employed to produce pure and crystalline precipitates and the precipitates so obtained also possess a better stoichiometry when compared to the precipitates obtained by the conventional method (Gordon *et al* 1959 ; Cartwright *et al* 1967). For example, copper cupferrate obtained by PFHS method can be weighed directly for the gravimetric determination of the metal (Heyn and Dave 1960) whereas the same obtained by the conventional method is to be ignited to oxide before weighing. Corsini and Abraham (1968) reported that the uranium quinolin-8-olate (uranyl oxinate) obtained by direct addition of the reagent was deficient in oxine. This red compound $\text{UO}_2(\text{C}_9\text{H}_6\text{ON})_2 \cdot \text{C}_9\text{H}_7\text{ON}$, which is usually employed for the analysis of uranium (VI) solutions was mentioned several times in literature (Hecht and Reich-Rohrwig 1929 ; Frere 1933 ; Fleck 1937 ; Classen and Visser 1946 ; Moeller and Wilkins 1953 ; Wendlandt 1956 ; Van Tassel and Wendlandt 1959, 1961 ; Bullwinkel and Nobel 1959 ; Horton and Wendlandt 1963 ; Tackett 1964 ;

Majee and Gordon 1965; Majee and Woodward 1966; Fleming and Lynton 1967; Milner *et al* 1960), but the deficiency of oxine was not observed. Similarly, the workers who studied the PFHS determination of uranium quinolin-8-olate by the hydrolysis of 8-acetoxyquinoline (Bordner *et al* 1961) and also by evaporation of mixed solvents (Howick and Rihs 1964) were not aware of this problem as Corsini and Abraham's (*loc. cit.*) work was published much later. On the other hand it was reported that the complex obtained by PFHS method had different compositions depending on the pH of the solution, a dark red compound $\text{UO}_2(\text{C}_9\text{H}_6\text{ON})_2$ $\text{C}_9\text{H}_7\text{ON}$ was obtained at pH 5.0 and an orange compound $(\text{UO}_2(\text{C}_9\text{H}_6\text{ON})_2)_2$ $\text{C}_9\text{H}_7\text{ON}$ resulted when the pH was increased to 6.8 (Bordner *et al* 1961). Hence the earlier observation of deficiency of oxine in the red compound may be due to the coprecipitation of the latter compound with the former.

Since PFHS methods produced stoichiometric precipitates which could be weighed directly unlike in conventional methods (Cartwright *et al* 1967; Siva Reddy and Krishna Reddy 1980) in the present investigation, uranium quinolin-8-olate has been precipitated from homogeneous solution by urea hydrolysis so as to remove the deficiency of oxine. Crystal sizes and thermal behaviour of the precipitates obtained by PFHS and conventional methods are compared.

2. Experimental

2.1. Reagents

All the chemicals used were of AnalaR grade, supplied by BDH. Uranium (VI) solution: About 8.5 gm of uranyl nitrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was transferred to a 1-litre flask, dissolved in water and diluted to the mark. The solution was standardised gravimetrically using diammonium uranate procedure (Vogel 1975). Quinolin-8-ol (oxine) solution: 2% solution (w/v) in acetone. Dilute nitric acid: Aqueous solution, 1 : 1 (v/v) of HNO_3 . Dilute ammonia solution: Ammonium hydroxide solution, 1 : 1 (v/v).

2.2. Apparatus

Elico pH-meter model LI-10 was used in the investigation. The sensitivity of the instrument is 0.05 pH units. The particle sizes were measured using Leitz-Wetzlar microscope and photomicrographs were also taken using the same microscope fitted with camera. The thermograms were recorded using a thermobalance supplied by Stanton Redcroft. The crucible used was made of alumina and the thermocouple employed was constructed from platinum and rhodium. The temperature was raised at the rate of 6° C/min. The samples were dried under vacuum for several days before recording the thermograms.

2.3. Procedure

An aliquot containing uranium (VI) was transferred into a clean 250 ml beaker and to it were added 10 gm of sodium acetate and 15 gm of urea. The initial pH of the solution was adjusted to 2.0 with 1 : 1 nitric acid. Quinolin-8-ol solution

5 hr. The solution was cooled to room temperature and the precipitate was filtered through a weighed sintered glass crucible of medium porosity, washed with warm water (ca. temperature 40° C) and dried for 1 hr at 115–120° C and weighed.

3. Results and discussions

3.1. Determination of uranium

Determination of uranium in the range 20–300 mg was successful and the results are presented in table 2. For a set of ten measurements of 81.25 mg of uranium (VI), the average amount and standard deviation were found to be 81.23 and 0.07 mg. For the same amount of uranium (VI), the amount found by bromometric procedure was 81.22 mg with a standard deviation of 0.12 mg. The microanalysis of the precipitate indicated the composition which correspond to $\text{UO}_2(\text{C}_9\text{H}_6\text{ON})_2 \cdot \text{C}_6\text{H}_7\text{ON}$ (table 1).

Table 1. Microanalysis of the complex.

Element	Theoretical percentage	Percentage obtained
C	46.03	45.95
H	2.72	2.68
N	5.97	5.97

Table 2. Determination of uranium.

Amount of uranium taken* mg	Amount of uranium found, mg ($n = 3$)	Difference mg ($n = 3$)
8.1 ₃	8.1 ₆	0.0 ₃
20.3 ₁	20.3 ₂	0.0 ₁
40.6 ₂	40.5 ₈	0.0 ₄
60.9 ₃	60.9 ₀	0.0 ₃
81.2 ₃	81.2 ₃	0.0 ₇ **
243.8	243.3	0.5
325.0	324.2	0.8

* Based on gravimetric (ammonium diuranate) procedure.

The results show that the complex is not soluble in quinoline oil. Even if the pH is increased beyond 9.0, it was observed that only dark red compound formed unlike in the earlier PFHS and conventional methods (Corsini and Abraham 1968; Bordner *et al* 1961; Howick and Rihs 1964). Moreover the complex possesses a good stoichiometry (no deficiency of oxine is observed). Addition of 2 to 3 fold excess of reagent did not affect the determination, though a slight excess ensured complete precipitation.

3.2. Particle size

The precipitate obtained is very dense and crystalline and higher amounts of uranium could be handled very easily. The distributions of particle sizes are given in table 3. The median value was obtained from the plots of particle size vs. logarithm of cumulative number. The median value calculated was $192 \times 112 \mu$. The precipitate obtained by conventional method is amorphous. The photomicrographs of the precipitate obtained are shown in figure 1.

3.3. Thermal behaviour

The thermograms are shown in figure 2. The precipitate obtained from homogeneous solution did not lose weight up to 200°C whereas the same obtained by conventional method was stable up to 180°C . The precipitate yielded unsolvated chelate on further heating due to the sublimation of supplementary quinolin-8-ol molecule and the *bis*-complex, $\text{UO}_2(\text{C}_9\text{H}_6\text{ON})_2$ was stable in the range of 240 – 310°C . At 440°C , the weight of the precipitate corresponded to U_3O_8 and from this temperature no weight loss was recorded. For the precipitate obtained by conventional method, the formation of *bis*-complex and oxide were observed at 220°C and 420°C respectively. The thermograms recorded in the present procedure agreed fairly well with the earlier ones but not with the pyrolysis curve recorded by Duval (1953) who stated that formation of U_3O_8 did not take place before 940°C .

Table 3. Distribution of particle sizes of the precipitate obtained by PFHS.

Total number of particles counted = 500

1 microscopic division = 16μ .

Lengthwise distribution		Breadthwise distribution	
Microscopic divisions	Percentage of distribution	Microscopic divisions	Percentage of distribution
1–10	64.7	1–4	52.6
11–20	16.8	5–8	18
21–30	11	9–12	15
31–40	5	13–16	6.6
41–50	2	17–20	5
51–60	0.5	21–24	2.2

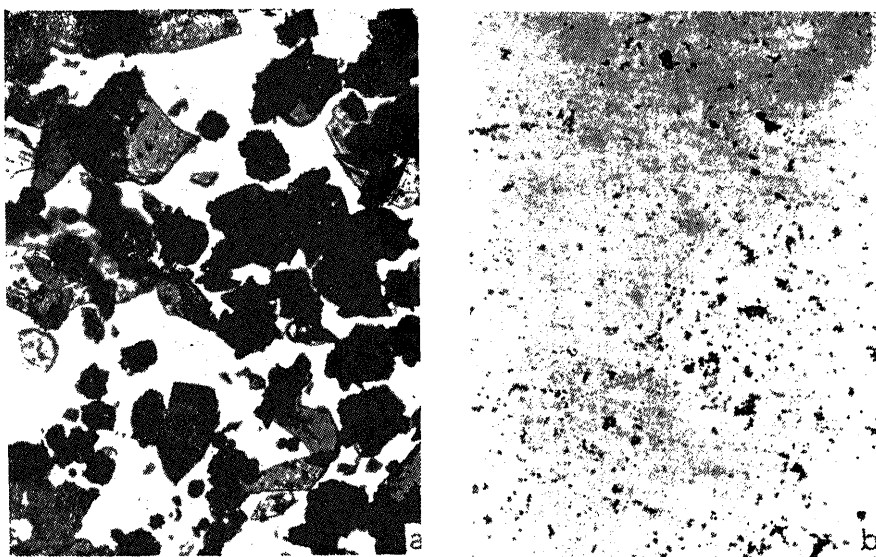


Figure 1. Photomicrographs of uranium quinolin-8-olate (a) from homogeneous solution, (b) by conventional method.

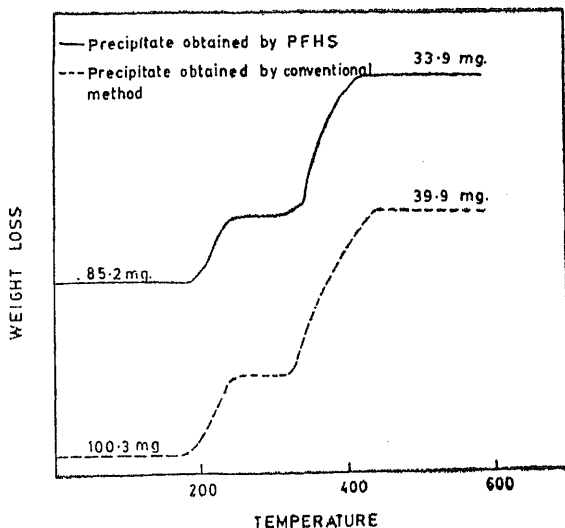


Figure 2. Pyrolysis of uranium quinolin-8-olate.

3.4. pH increase in presence of various anions

The function of the anion in urea hydrolysis is three fold ; (i) buffer action, (ii) complex formation and (iii) incorporation of anion in the precipitate and formation of basic salt. In the precipitation of hydroxides and basic salts, the anions help in the formation of basic salts though other reasons are not ruled out (Cartwright 1967). Similarly in the precipitation of neutral salts or complexes, the anion serves mainly as buffer, though complex formation is not ruled out (Siva Reddy and Krishna Reddy 1979). This can be understood only from the plots of pH increase with time and percentage recovery of the metal with pH in presence of various anions. pH increase in the presence of various anions is shown in figure 3 and the percentage recovery of uranium (VI) with pH is given in figure 4. pH increase is very rapid in the presence of ammonium chloride, ammonium sulphate, tartaric acid and succinic acid and slow in the presence of acetate and formate buffers. A very crystalline precipitate is obtained in the presence of sodium acetate and ammonium acetate. The pH increase with time shown in figure 3 is for nearly 80 mg of uranium (VI), 15 ml of quinolin-8-ol solution and 10 gm of buffer. Each value represented in the figure is the average for six experiments. From the plot of percentage recovery of uranium with pH (figure 4), it is seen that the initial precipitation process is delayed in the presence of succinic acid and EDTA due to complex formation other buffers appear to control pH raise only.

3.5. Effect of diverse ions

When precipitation was carried out in the presence of EDTA, 100 mg each of copper (II), iron (III), zinc (II), cadmium (II), lead (II), aluminium (III) and

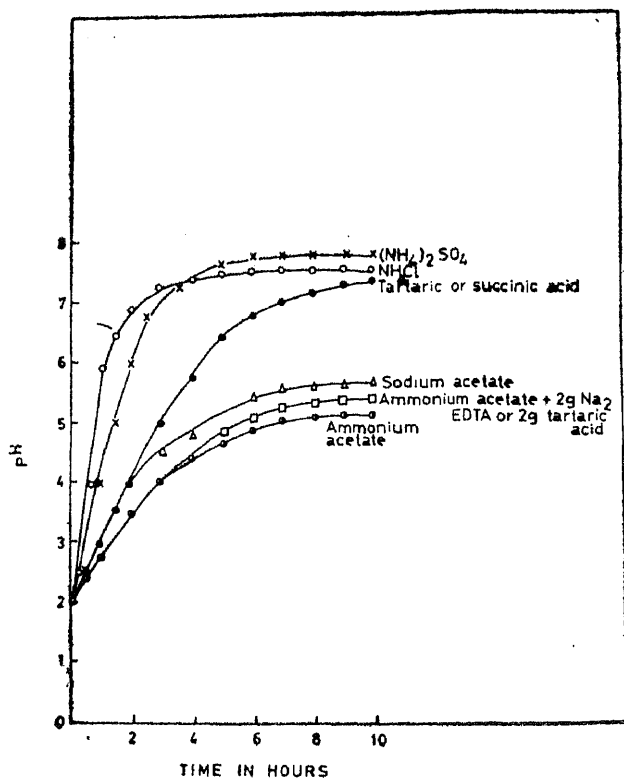
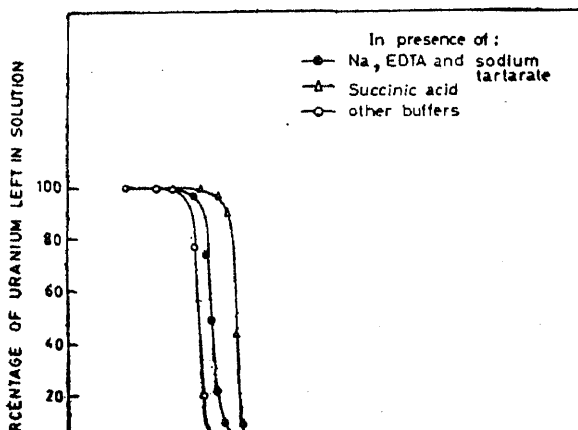


Figure 3. pH increase with time in presence of various buffers.



Initial molarity of EDTA in the solution = 0.04 M
Amount of cation added = 100 mg.

Cation added	Amount of uranium found for 81.2 mg of uranium taken mg	Difference mg
Copper(II)	81.2 ₀	0.0 ₅
Nickel(II)	81.1 ₈	0.0 ₇
Iron(II)	81.3 ₂	0.0 ₇
Manganese(II)	81.2 ₀	0.0 ₅
Zinc(II)	81.2 ₀	0.0 ₅
Cadmium(II)	81.1 ₈	0.0 ₇
Lead(II)*	81.3 ₄	0.0 ₉
Aluminium(III)	81.3 ₂	0.0 ₇
Thorium(IV)*	81.2 ₈	0.0 ₇

* Added in the form of nitrates.

Other salts are added in the form of sulphates.

4. Conclusion

From the above discussion, it is clear that the PFHS determination of uranium by urea hydrolysis is accurate. No deficiency of quinolin-8-ol (oxine) or differences in compositions has been observed unlike in earlier conventional and PFHS methods. The highly crystalline precipitate obtained in the present method facilitated easy filtration and less interference from impurities.

Acknowledgements

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R PAYNE and R J MAGEE*

Department of Inorganic and Analytical Chemistry, La Trobe University, Bundoora, Melbourne, Victoria, Australia 3083

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Abstract. The complexes formed in the interaction of the copper(II) ion with glucuronic acid over the pH range 4.0–11.0 were investigated using d.c. polarography, cyclic voltammetry and chronoamperometry. It was found that below about pH 6.1 no complex forms, while in the pH range of approximately 6.2–7.4 and again 7.5–9.8 stable complexes were formed in solution. At high pH values, the complexes appear to break up. The complex formed in the pH range 6.2–7.4 was studied and stability constants determined by two different methods.

Keywords. Electrochemical investigation; polarography, cyclic voltammetry; stability constants; copper(II) glucuronate.

1. Introduction

In investigations on the uptake of copper by certain bacteria (Payne *et al* 1981) a copper complex of glucuronic acid was isolated and the structure compared with that of model compounds. As a result of these investigations, it became necessary to investigate the interaction of copper(II) ions with glucuronic acid over a wide pH range. This study was carried out using electrochemical techniques. While a number of reports have appeared (Biswas *et al* 1978; Rajan and Martell 1967) on the polyhydroxy acids and their complexes with Cu(II), particularly citric and tartaric acids, little work has been reported on the copper complexes of the uronic acids in general and glucuronic acid in particular. Makridou *et al* 1977 have studied the formation of complexes of the types MA and MA' between different metal ions, including Cu(II), and glucuronic acid and galacturonic acid by a potentiometric method. They determined stability constants and concluded that the metal complexes of galacturonic acid are more stable than those of glucuronic acid.

In the present paper, the results of a study on the formation of complexes between the Cu(II) ion and glucuronic acid, using polarography methods, are presented.

2. Experimental

The polarographic, cyclic voltammetric and chronoamperometric studies were carried out on the AMEL 471-Multipolarograph System and the Princeton Applied

*To whom all correspondence should be made.

Research (PAR) 170 Electrochemistry System. Results were plotted on a Hewlett-Packard 7040A X-Y Recorder. pH was recorded on an ET1572 Digital pH meter. The polarographic cell had a three electrode configuration consisting of a saturated calomel reference electrode and a platinum counter electrode. For the d.c. polarographic measurements a glass capillary dropping electrode (DME) was used : for the cyclic voltammetric and chronoamperometric measurements the hanging mercury drop electrode (HMDE) was used. Experiments were also carried out using a glassy carbon electrode. All polarographic and cyclic voltammetric data were obtained at $25 \pm 0.02^\circ \text{C}$, solutions being deoxygenated with pre-dried, oxygen-free nitrogen.

Sodium glucuronate was either prepared by direct titration of the acid with sodium hydroxide solution or was purchased directly (Sigma Chemicals). In both cases, the product was recrystallised. Copper nitrate was used as the source of Cu(II) ions. Stock solutions of copper nitrate were standardized by titration with EDTA using a potentiometric end-point determination. All results were obtained at an ionic strength of 0.74 M (NaClO_4). pH values were checked before and after recording voltammograms.

3. Results and discussion

3.1. Polarographic investigations

3.1a *Effect on $E_{1/2}$ of variation in pH* : With the polarographic cell containing $6.25 \times 10^{-3} \text{ mol dm}^{-3} \text{ Cu}^{2+}$, a ligand concentration of $0.237 \text{ mol dm}^{-3}$ and 0.5 mol dm^{-3} of NaClO_4 , the pH was varied over the range $4.0-9.8$. In each case, polarograms were obtained in the potential range $+0.2$ to -0.700 volt . In the range pH 4.0 to about 6.3 or 6.4 , one wave (wave I) was obtained with an $E_{1/2}$ value around -0.02 to -0.03 volt and was clearly indicative of Cu(II) in a 2-electron reduction step. Around pH 6.4 , a second wave (wave II) began to appear in addition to and following wave I. As the pH was increased, wave II increased steadily in height, while wave I decreased in height. Maximum development of wave II appears to be around pH 7.4 . At this pH, a very small residual first wave (wave I) at $E_{1/2} \cong -0.036 \text{ volt}$ still persisted with wave II showing an $E_{1/2}$ around -0.14 volt . However, beyond pH 7.4 , the residual first wave disappeared and a third wave (wave III) now began to develop more negative than wave II ($E_{1/2} \cong -0.36 \text{ volt}$). Both wave II and wave III existed together up to about 9.8 : however, wave II gradually decreased in height, while wave III increased in height with increasing pH. At high pH values, waves II and III disappeared and a new wave (wave IV) with $E_{1/2}$ around $+0.102$ developed. Examples of the development of the waves mentioned above are shown in figure 1 (a), (b), (c), (d).

In the pH range $4.0-6.3$, the single wave (wave I) present was shown to be due to the reduction of free Cu^{2+} ion (figure 1a) i.e., no complex is formed in acidic solution between Cu^{2+} and glucuronic acid. In the range pH $6.4-7.4$, the first wave is due to reduction of Cu^{2+} , while the second wave (wave II) is indicative

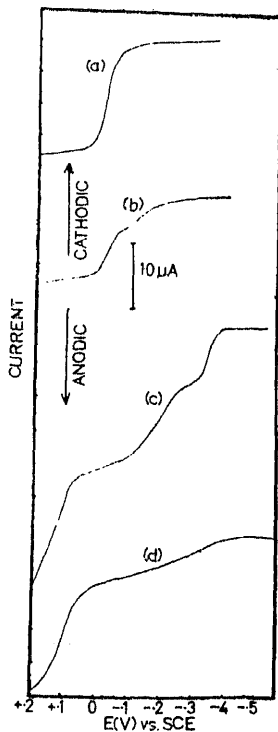


Figure 1. D.C. polarograms at DME at varying pH values of Cu(II) glucuronate complexation in aqueous solution, 0.5 M NaClO₄. (a) pH = 5.74 ; (b) pH = 6.4 ; (c) pH = 8.70 ; (d) pH = 9.70. $T = 25^{\circ}\text{C}$; $h = 62.0\text{ cm}$; 0.004% Triton x-100 added.

appearance of wave IV appears to be indicative of the ligand itself. To check this assumption, polarograms of the ligand were obtained. At pH 11.0, a wave was obtained identical to that obtained for the solution which had the copper complex present (figure 1d). It is concluded that this wave may be due to the reduction of the ligand or a mercury complex formed by the ligand. It would appear then that at high pH values any copper complexes formed at lower pH values break up releasing the ligand.

3.2. Wave II

3.2a. *Variation of limiting current with height of Hg column* : Using the same concentration of Cu²⁺, ligand and NaClO₄ as for the investigation of the effect of pH on $E_{1/2}$, the effect of the height of the mercury column on the limiting current of the copper complex formed around pH 7.4 was examined. Limiting currents for wave II were found to be proportional to $\sqrt{h}$ indicating diffusion control under the polarographic conditions.

E vs $\log (i/id - i)$ gave a linear plot from which the slope (average of a series of results) was found to be -87 mv, indicating a quasi-reversible reduction. Assuming a value of a not too different from 0.5 , gives a value of $n \cong 2$ for the number of electrons involved in the reduction.

3.2c. $E_{1/2}$ vs $\log C(x)$: With the pH at 7.4 , the effect of change in the concentration of ligand on $E_{1/2}$ was examined. A linear plot was obtained indicating the presence of a single complex at this pH. From the relationship

$$\Delta E_{1/2} = \frac{0.0591}{n} \log \beta - \frac{0.0591}{n} p \cdot \log (C(x)).$$

the value p (number of ligands coordinated to metal ion) and $\log \beta$ were determined using the slope and intercept of the straight line plot.

The value obtained for p was approximately 2 (1.85). For the stability constant determination ($\log \beta$), a standard pH titration method was also carried out for comparison with the polarographic method and the copper complexes of glutamic acid were also determined by both methods. The basis of the pH titration method, as given by Albert and Sargent (1971) is that the average number of ligands bound by one atom of the metal is defined as

$$\bar{n} = \frac{\text{moles of bound ligand}}{\text{total moles of Cu}^{2+}} = \frac{[\text{Cu}(\text{gluc})^+] + 2[\text{Cu}(\text{gluc})_2]}{[\text{Cu}^{2+}] + [\text{Cu}(\text{gluc})^+] + [\text{Cu}(\text{gluc})_2]}.$$

This may be re-written in terms of stability constants as

$$\bar{n} = \frac{K_1(\text{gluc}^-) + 2K_1K_2(\text{gluc}^-)^2}{1 + K_1(\text{gluc}^-) + K_1K_2(\text{gluc}^-)^2} = \frac{\beta_1(\text{gluc}^-) + 2\beta_2(\text{gluc}^-)^2}{1 + \beta_1(\text{gluc}^-) + \beta_2(\text{gluc}^-)^2}.$$

On re-arranging we get

$$\frac{\bar{n}}{(1 - \bar{n})(\text{gluc}^-)} = \beta_1 + \frac{(2 - \bar{n})(\text{gluc}^-)}{(1 - \bar{n})} \beta_2.$$

A plot of $\bar{n}/(1 - \bar{n})(\text{gluc}^-)$ vs $(2 - \bar{n})(\text{gluc}^-)/(1 - \bar{n})$ should give a straight line of intercept β_1 and slope β_2 .

In the present work, a computer was used to determine the stability constants instead of using the graphical plot. Results are shown in table 1.

Table 1. Stability constants of Cu(II) glucuronate and glutamate.

Complex	Method				Literature values
	Polarography		pH titration		
Cu glucuronate	$\log \beta_1$	..	1.01	1.48	Makridou <i>et al</i> 1977
	$\log \beta_2$	4.100	4.103	..	
Cu glutamate	$\log \beta_1$	..	8.314	8.20	

Table 2. Effect of pH on $E_{1/2}$ value of wave II.

pH	$E_{1/2}$	pH	$E_{1/2}$
6.3	..	7.05	-0.147
6.5	-0.094	7.15	-0.150
6.7	-0.136	7.25	-0.154
6.85	-0.141	7.5	-0.161
6.95	-0.143	8.1	

3.2d. $E_{1/2}$ vs pH : For wave II, the pH was varied from the value at which the wave first appeared until its disappearance at the higher pH. For each pH the $E_{1/2}$ value was determined. The variation of $E_{1/2}$ with pH is shown in table 2. From the plot of $E_{1/2}$ vs pH a straight line resulted. Now,

$$E_{1/2} = E^0 - \frac{0.0591}{n} m \text{ pH} + \frac{0.0591}{n} \log \left(\frac{f_o C_o}{f_r C_r} \right).$$

Thus, from the slope of the plot which is equal to $-0.591/n \cdot m$, m = number of hydrogen ions involved may be determined. The average of a number of experiments gave a value of $m \cong 2$.

3.3. Wave III

As indicated earlier, this wave which appears above pH 7.5 may possibly be the result of the formation of a second complex. Attempts were made to apply the same sort of tests to it as applied to wave II. However, difficulties were always experienced in deciding the point at which the wave began as it followed so closely on wave II. Log plot analyses indicated a value between 1 and 2 electrons for the number of electrons involved in the reduction and there was evidence for considerable irreversibility.

4. Cyclic voltammetry

Cyclic voltammograms were obtained at varying pH values, under the same conditions as used for the d.c. polarographic studies discussed above. Figure 2 (a), (b), (c) shows the results obtained. Below pH $\cong 6.1$, a voltammogram with one cathodic peak and one anodic peak (figure 2a) was obtained. This voltammogram showed clearly that only free Cu^{2+} ions were present in the solution. Above pH 6.3 a second cathodic peak appeared and by pH 7.4 this was the only cathodic peak; the first wave due to Cu^{2+} had disappeared. Figure 2b shows the voltammogram at pH 7.4. The cathodic peak at E_p approximately -0.14 volt corresponds to reduction of the same copper complex observed in the polarographic study at this pH. The anodic peak (I_{pa}) corresponds to the main reduction wave (I_c) and indicates a quasi-reversible electrode reaction in

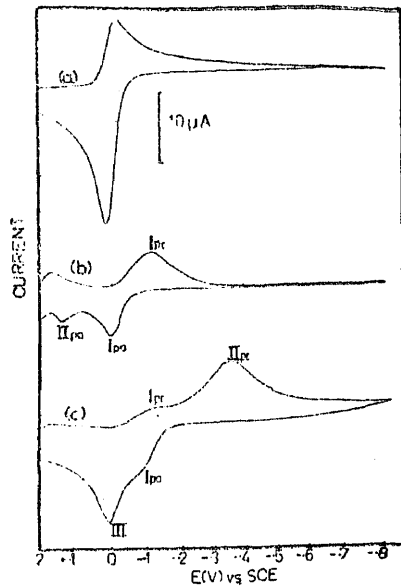


Figure 2. Cyclic voltammograms at HMDE (scan rate — 20 mV/sec, $T = 25^\circ \text{C}$) in aq. solution, 0.5 M NaClO_4 in presence of nitrogen at varying pH values. (a) pH = 5.74; (b) pH = 7.40; (c) pH = 8.70.

for which there is no corresponding cathodic wave was found and is thought to be due to oxidation of the ligand or a mercury complex of free ligand. Accordingly, cyclic voltammograms were obtained for the free ligand. As expected, a peak was obtained exactly at the same peak potential as the anodic peak in figure 2b, confirming that this peak is caused by oxidation of the ligand.

The data for peak I_{po} at different scan rates is shown in table 3. Figure 2c shows the cyclic voltammogram at pH 8.5 of the copper-glucuronic acid system. Two cathodic peaks are present, the first, very small one at $E_p \approx -0.14$ (I_{po}) representing a residual part of the complex which forms between pH 6.1 and 7.4. The second cathodic peak with E_p around -0.4 (II_{po}) is the major peak in the voltammogram and represents the complex which forms at pH values greater than 7.4. The absence of a corresponding anodic peak for the cathodic peak II_{po} indicates that the electrode reaction is irreversible. For the small cathodic peak, I_{po} , a corresponding anodic peak is discernible (I_{po}) as a shoulder on a larger anodic peak (III_{po}). This again indicated the quasi-reversible nature of the electrode reaction of this complex. The large anodic peak (III_{po}) found in the voltammograms is of interest. There appears to be no corresponding cathodic peak at any scan rate. Initially it was supposed that it was due to oxidation of free ligand or a mercury complex of the ligand. However, experiments carried out with the free ligand indicated that it was not a ligand peak. On further investigation, it was found that this peak of sharp symmetry increased in magnitude with increasing scan rate and decreasing concentration, thus showing charac-

Table 3. Effect of voltage scan rate on wave II.

Scan rate V sec ⁻¹	E_{p_0} vs SCE 0.005 V	E_{p_a}	ΔE_p (mV)	I_{p_0}	I_{p_a}	$\frac{I_{p_a}}{I_{p_0}}$
0.002	-0.144	-0.064	80	0.425	0.689	1.62
0.005	-0.148	-0.064	84	0.453	0.709	1.57
0.01	-0.156	0.068	88	0.709	0.709	1.00
0.02	-0.154	-0.062	92	0.866	0.778	0.898
0.05	-0.158	-0.065	93	0.900	0.720	0.800
0.10	-0.160	-0.066	94	1.024	0.787	0.762
0.20	-0.180	-0.060	118	1.732	1.339	0.760

5. Chronoamperometry

Chronoamperograms were recorded for the complex formed around pH 7.4 by applying a voltage on the plateau of wave II to the HMDE. The derived "current versus time^{-1/2} plot" was a straight line. This linear i versus $t^{-1/2}$ plot shows that the electrode reaction responsible for wave II is diffusion controlled and that there is no preceding chemical reaction coupled with the electron transfer process.

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Molecular constants of PSF_3 and NSF_3

A NATARAJAN* and S SOMASUNDARAM

Department of Physics, Autonomous Post-Graduate Centre, Tiruchirapalli 620 020, India

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Abstract. A complete vibrational analysis of PSF_3 and NSF_3 molecules is described in this paper. Urey-Bradley and General valence Force Fields have been computed for these molecules, belonging to C_{3v} symmetry using the fundamental frequencies obtained from infrared spectra. The mean square amplitudes, Coriolis coupling coefficients and centrifugal distortion constants have also been calculated and presented here.

Keywords. Symmetry; vibrational frequencies; normal coordinate analysis; molecular constants.

1. Introduction

The molecules PSF_3 and NSF_3 possess C_{3v} symmetry. Their fundamental frequencies are distributed accordingly as $3a_1 + 3e_1$.

Considerable amount of work has been done on the spectra of PSF_3 . Normal coordinate analysis has been carried out by Shurvell (1969) and Koniger and Muller (1977). Recently fresh vibrational assignments have been made for PSF_3 and NSF_3 by Koniger *et al* (1979) and they are used for the present work. The internal coordinates, numbering of atoms and the orientation of Cartesian coordinate axes of these molecules are shown in figure 1.

Normal coordinate analysis has been performed by Koniger *et al* (1979) using the general valence force field (GVFF). However, the GVFF has been repeated and in addition Urey-Bradley force field (UBFF) has also been worked out. The mean square amplitudes of vibration, the generalized mean square amplitudes of vibrations, shrinkage constants, Coriolis coupling coefficients and centrifugal distortion constants have been computed and reported here.

2. Theoretical considerations

2.1. Molecular force field

UBFF and GVFF are used to obtain the force constants. A reliable set of force constants has been obtained by Wilson's (1939) F - G matrix formalism.

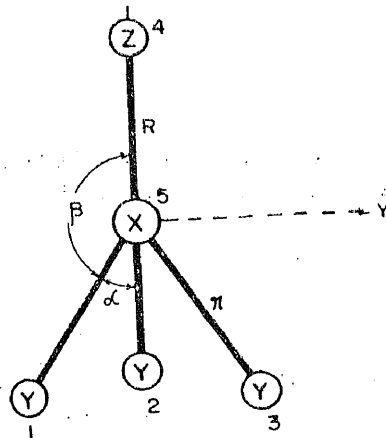


Figure 1. The orientation of Cartesian coordinate axes, the numbering of atom and the internal coordinates of XY_3Z (pyramidal) type of molecules.

2.2. Mean square amplitudes of vibration

The symmetrised mean square amplitude matrix Σ has been evaluated using the relation (Cyvin 1960)

$$\Sigma = L \Delta L',$$

where the L 's are the characteristic vectors and Δ is a diagonal matrix consisting of the mean square values of the normal coordinates given by Block (1932). The generalised mean square amplitudes (Morino and Hirota 1955) $\langle(\Delta Z)^2\rangle$, $\langle(\Delta X)^2\rangle$ and $\langle(\Delta Y)^2\rangle$ have been evaluated using the Σ matrix from the relation

$$X = AS,$$

where

$$A = M^{-1} B' G^{-1}.$$

2.3. Coriolis coupling coefficients

The active couplings for these molecules are $a_1 \times e$ and $e \times e$ belonging to ζ'' and ζ^z respectively. The Coriolis coupling coefficients have been calculated from the relation given by Meal and Polo (1956)

$$\zeta^a = L^{-1} C^a (L')^{-1},$$

where C^a matrix is obtained from the geometry and atomic masses.

2.4. Centrifugal distortion constants

The centrifugal distortion constants have been computed using the relations given by Kivelson and Wilson (1952, 1953), and by Cyvin *et al* (1968).

To check whether the chosen set of symmetry coordinates contributes maximum to the potential energy associated with the normal coordinates of the molecule, the P.E.D. was calculated using the relation

$$V_{ik} = \frac{100 \cdot F_{ik} L_{ik}^2}{\lambda_k}.$$

It is found (table 1) that the contributions to the main diagonal elements are predominant which confirms that the chosen coordinates form a normal mode representation.

3. Results and discussion

The molecular parameters, the observed and calculated frequencies of the fundamentals are given in table 1. The valence force constants in GVFF and the Urey-Bradley force constants are presented in table 2. The values agree very well with those calculated by Koniger *et al* (1979). The N-S force constant in NSF₃ molecule is found to be 12.683 m dyne/Å in general valence and 12.369 in UBFF. This indicates the double bond nature of the N-S bond.

It is slightly larger than f_{N-S} in other molecules such as NSCl [f_{N-S} : 10.57 m dyne/Å, Namasivayam and Nair 1978; 10.15 m dyne/Å, Peacock *et al* 1969; 10.41 m dyne/Å, Nagarajan *et al* 1967]. This may be due to the delocalisation of electrons in the N-S bond region and consequently enhancement of nitrogen-sulphur back donation of electron density. This results in the reduction of such back donation from fluorine to sulphur. Hence the f_{S-F} is comparatively small.

The mean square amplitude quantities at 300 K calculated using Σ matrix elements are presented in table 3. The mean amplitudes of vibration at 300 K for bonded and non-bonded distances are given in table 4, and the generalised mean square amplitudes (both parallel and perpendicular) of vibration along with the shrinkage constants are given in table 5. The mean amplitudes of vibration for non-bonded distances are larger than those for bonded distances. The Coriolis coupling coefficients of PSF₃ and NSF₃ molecules are listed in table 6. The Coriolis coupling between the two degenerate modes of the fundamentals ν_4 and ν_5 are fairly strong for rotation about the Z axis. The Coriolis coupling coefficients satisfy the sum rule

$$\sum_{i=4}^6 \zeta_{it}^2 = \frac{I_A}{2I_B}$$

where I_A and I_B are the principal moments of inertia whose calculated values are also given in table 1. The calculated values of ζ_{44}^2 , ζ_{55}^2 and ζ_{66}^2 agree very well with the experimental values obtained by Koniger *et al* (1979) in the band contour analysis of the spectra and also with the experimental values investigated in the microwave analysis by Small and Smith (1976). These values are also given in table 6 for comparison. The coupling between ν_4 and ν_5 is very strong in PSF₃

Table 1. Observed and calculated frequencies (cm^{-1}), molecular parameters and PED of NSF₃ and PSF₃.

	Obs.	NSF ₃		Obs.	PSF ₃		PED
		Cal.	PED		Cal.	PED	
a_1							
ν_1	1522.7	1521.8	$93.52 S_1 + 6.48 S_4$	695.5	695.3	$73.91 S_1 + 24.46 S_2 + 1.63$	
ν_2	772.0	771.6	$0.40 S_1 + 98.53 S_2 + 1.10 S_4$	985.0	984.8	$4.77 S_1 + 93.99 S_2 + 1.24$	
ν_3	522.9	522.6	$0.10 S_1 + 0.70 S_2 + 99.20 S_3$	441.8	441.2	$14.87 S_1 + 2.17 S_2 + 82.96$	
e_1							
ν_4	817.4	817.0	$98.03 S_4 + 1.16 S_5 + 0.81 S_6$	947.0	947.3	$80.08 S_4 + 18.02 S_5 + 1.99$	
ν_5	429.8	429.0	$1.59 S_4 + 91.28 S_5 + 7.13 S_6$	404.7	404.2	$1.09 S_4 + 92.56 S_5 + 6.3$	
ν_6	342.2	342.0	$3.50 S_4 + 0.84 S_5 + 95.66 S_6$	274.8	274.3	$0.70 S_4 + 1.54 S_5 + 97.7$	
$R(X-Z)$	1.416 Å			1.86 Å			
$r(X-Y)$	1.552 Å			1.43 Å			
$a(Y\hat{X}Y)$	94.03°			100.3°			
$\beta(YXZ)$	122.36°			117.2°			
I_x amu Å	97.98			104.9			
$I_y = I_z$ amu Å	16.39			196.1			

Valence force constants			Urey-Bradley force constants		
	PSF ₃	NSF ₃		PSF ₃	NSF ₃
f_R	5·8521	12·6830	K_R	5·8269	12·3692
f_r	6·2036	4·8850	K_r	6·2181	4·5541
f_{rr}	0·3410	0·2620	H_α	0·6759	0·6043
f_{rr}	0·4363	0·1218	H_β	0·4287	0·2532
$f_\alpha-f_{\alpha\alpha}$	0·5390	0·7210	f_{yy}	0·2349	0·2252
$f_\beta-f_{\beta\beta}$	0·7338	0·3190	f_{yz}	0·1762	0·1410
$f_{R\beta}$	0·7243	0·3372			
$f_{r\beta}$	0·6362	0·4131			
$f_{r\alpha}$	0·0411	0·1862			
$f_{\alpha\beta}$	-0·0237	-0·0460			

Table 3. Mean square amplitudes of vibration of PSF₃ and NSF₃ at 300 K (10⁻⁴ Å²).

	PSF ₃	NSF ₃
σ_R	16·0720	11·5866
σ_r	12·9593	17·9935
σ_{rr}	- 0·7306	- 0·4385
σ_{rr}	- 1·2124	- 1·2126
$\sigma_\alpha-\sigma_{\alpha\alpha}$	94·3682	119·6820
$\sigma_\beta-\sigma_{\beta\beta}$	81·3021	131·1066
$\sigma_{r\alpha}$	- 8·1070	- 3·3928
$\sigma_{r\beta}$	- 5·2334	- 7·9621
$\sigma_{R\beta}$	- 2·3510	- 5·9198
$\sigma_{\alpha\beta}$	17·6240	8·7983

Table 4. Mean amplitudes of vibration (Å) of bonded and nonbonded distances of PSF₃ and NSF₃ at 300 K.

	PSF ₃	NSF ₃
l_{x-y}	0·0401	0·0340
l_{x-z}	0·0360	0·0424
$l_{x\dots x}$	0·0723	0·0764
$l_{y\dots z}$	0·0427	0·0716

Molecule	Atom Pair	Parallel $\langle (\Delta z)^2 \rangle$	Perpendicular		Shrinkage
			$\langle (\Delta x)^2 \rangle$	$\langle (\Delta y)^2 \rangle$	
PSF ₃	P—S	16.0712	27.3312	27.3312	..
	P—F	12.9521	29.6321	41.2213	..
	F...F	52.2830	16.3217	37.9424	0.0026
	S...F	18.2137	23.1522	36.5628	0.0082
NSF ₃	N—S	11.5832	21.7372	15.4000	..
	S—F	17.9922	53.5862	68.2162	..
	F...F	58.3631	134.6021	154.2133	0.0052
	N...F	51.2216	72.1325	83.2165	0.0093

Table 6. Coriolis coupling coefficients of PSF₃ and NSF₃ molecules.

Coupling $a_1 \times e$:	PSF ₃	NSF ₃
ζ_{14}	0.6724	0.3453
ζ_{15}	-0.6631	-0.3112
ζ_{18}	0.0492	0.5138
ζ_{24}	-0.2961	-0.2191
ζ_{25}	0.1276	0.8465
ζ_{28}	0.3149	0.1049
ζ_{34}	0.3911	0.1739
ζ_{35}	0.3462	0.0332
ζ_{38}	-0.5228	-0.5082
Coupling $e \times e$		
ζ_{44}^*	0.5813	0.5612
	(0.57)*	(0.5)*
	(0.59)**	
ζ_{55}^*	-0.5891	-0.2330
	(-0.56)*	(-0.2)*
	(-0.49)**	(-0.2256)*
ζ_{68}^*	0.2592	0.1482
	(0.26)*	(0.15)*
	(0.16)**	(0.1567)†
ζ_{45}^*	-0.6525	0.4070
ζ_{48}^*	0.5441	0.6066
ζ_{58}^*	0.4631	-0.0177

* band contour analysis ; Koniger *et al* (1979), ** spectral analysis : Clark and Ellestad (1976)

† microwave analysis ; Small and Smith (1976)

Table 7. Centrifugal distortion constants of PSF_3 and NSF_3 molecules (cm $^{-2}$).

	PSF_3	NSF_3
D_J	1.0678 (1.082)*	0.2971 (0.2742)*
D_K	-1.4735	-1.1863
D_{JK}	1.9763 (1.9047)*	1.9363 (1.961)*

Band contour analysis: Koniger *et al* (1979)

The centrifugal distortion constants are presented in table 7. Since these molecules are symmetric tops, the centrifugal stretching coefficients R_5 , R_6 and δ_J vanish and the other coefficients D_J , D_K and D_{JK} have been evaluated. These values agree very well with those obtained by Koniger *et al* (1979) in the band contour analysis.

Conclusion

It is expected that the analysis presented here would help us in knowing the spectroscopic properties of these molecules. The mean amplitude calculations are useful in the interpretation of electron diffraction studies in the molecular structure determinations and the shrinkage constants are helpful in the refinement of bond lengths obtained experimentally. The Coriolis constants are used in the interpretation of vibration-rotation spectra of these molecules. The centrifugal distortion constants calculated here for NSF_3 will be useful in the study of microwave spectra of the molecule.

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High resolution electron microscopy of chloritoid minerals from different geological melieu

G N SUBBANNA and G V ANANTHA IYER*

Materials Research Laboratory and Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

MS received 14 December 1981

Abstract. Structural defects of three chloritoid minerals from distinct geologic melieu have been investigated by high resolution electron microscopy. X-ray powder and electron diffraction patterns indicate that the chloritoid from one geological source (A) is $2M_1 + 2M_2$ monoclinic variant while those from another geological source (B) are $2M_2$ monoclinic variants. In a typical one-dimensional lattice image of a crystal from source A, the $2M_2$ matrix is broken by insertion of triclinic intergrowths. Another crystal with the $2M_2$ matrix showed single, triple, quadruple and quintuple layers displaying an unusually high degree of disorder. Lattice images of $2M_2$ monoclinic variants from source B yielded more homogeneous micrographs.

The important finding from the present studies is that the chloritoid from source A is a severely disordered low-temperature intermediate phase in the conversion of the triclinic chloritoid to the high-temperature ordered monoclinic variants of source B. Severely disordered chloritoids, marking the beginning of low grade metamorphism, are generated as intermediates between the state of complete disordered arrangement towards the end of low grade metamorphism within the narrow stability range of 400°–500° C.

Keywords. Chloritoid mineral; electron microscopy; lattice images; different geological melieu.

1. Introduction

Fine details of mineral structures have long been successfully obtained by x-ray diffraction techniques. In spite of the unquestioned power of x-ray crystallography, there is no way we can obtain direct information on the ultramicrostructure of solids by this technique. High resolution transmission electron microscopy is well suited for the study of deviations from perfect periodicity in minerals because it provides direct interpretable lattice images down to 2 Å resolution. Thus, column defects, stacking faults and intercalation of different structural units have been examined by the lattice imaging technique (Anderson 1978). During the last few years there have been many studies utilising high resolution electron microscopy to study minerals (e.g. see Hutchison *et al* 1977; Thomas *et al* 1979; Buseck 1979). We considered it worthwhile examining lattice images of a mineral

* To whom all correspondence should be made.

from different sources to find out how the geological history affects the ultra-micro-structure and whether the observed ultra-microstructure can reveal the mechanism of reactions occurring during metamorphism. For this purpose we have investigated samples of chloritoid occurring in two different parts of Karnataka South India, having distinct geological environments. An attempt has been made to correlate the observed structure with the thermal history.

2. Experimental

Of the three chloritoids selected for the present study one (KB 7543) is from Kibbanahalli belt east of Banasandra ($13^{\circ} 15'$, $76^{\circ} 41'$), Tumkur district of Karnataka and the other two samples (HN 7801 and HN 7808) are from Shingarana-halli ($12^{\circ} 52'$: $76^{\circ} 15'$) and Haradanahalli ($12^{\circ} 51'$: $76^{\circ} 14'$) both situated north east of Holenarasipur belt in Hassan District of Karanataka. We designate Kibbanahalli and Holenarasipur belts as sources *A* and *B* respectively. KB 7543 chloritoid occurs in a greenish buff coloured highly fissile rock as dark thin prismatic crystals along restricted foliation planes. The coexisting minerals in the rock are chlorite, mica and quartz. HN 7801 occurs as dark stubby porphyroblast upto a cm in size, in a light green foliated rock with phengite and chlorite. HN 7808 chloritoids are dark stubby porphyroblast crystals occurring in a matrix of olive green chlorite and with almandine garnet. The chloritoid crystals from the rock specimens could easily be separated. They were crushed, powdered and pure fractions were obtained using heavy liquids like bromoform and methylene iodide. The chemical analyses data of the samples are given in table 1. X-ray powder diffraction analysis were carried out with Philips x-ray diffractometer using CoK radiation. The unit cell constants determined from x-ray studies are comparable with the cell constants reported by Jefferson and Thomas (1978).

Table 1. Chemical composition of the chloritoids.

Sample No.	KB 7543	HN 7801	HN 7808
SiO ₂	25.41	26.49	24.08
TiO ₂	1.02	1.23	1.88
Al ₂ O ₃	33.89	39.98	35.03
Fe ₂ O ₃	4.01	3.12	6.04
FeO	26.68	19.52	21.63
MnO	1.04	0.84	0.92
MgO	0.95	1.82	2.89
CaO	0.07	0.05	0.08
Na ₂ O	0.14	0.19	0.30
K ₂ O	0.05	0.04	0.01
H ₂ O ⁺	6.58	6.66	6.98
H ₂ O ⁻	0.05	0.05	0.04
Total	99.99	99.82	99.89

A double tilt holder was used for orienting the crystals such that C^* axis is perpendicular to the electron beam. 70 μm as well as 50 μm objective apertures were used for forming the image and through-focus images were recorded at various focussing conditions for all specimens. Generally an underfocus of about 80 nm relative to the Gaussian image is necessary to obtain images of optimum contrast which could be directly interpretable in terms of the structure of the crystal and of the defects within it. Since the main aim in this study is to determine the deviations from perfect periodicity in chloritoid minerals obtained from different geological milieu by direct imaging of non-periodic features to characterise the structure type and their intergrowths, one-dimensional lattice images are sufficient to investigate the stacking disorders. Chloritoids cleave on (110) as well as (001) planes, and a crystal could be easily oriented with one of the principal axes normal to the beam. With the goniometer stage ($\pm 25^\circ$ max tilt) fitted to the Philips EM 301 electron microscope used for the study it was possible to record images of only one section even though in principle it is possible to obtain images from the next section by tilting the crystal through 30° . This limitation is partly due to insufficient tilting and also due to increase in crystal thickness after tilting it through 30° . The imaging code was established experimentally from the analysis of characterised species following the method of Jefferson and Thomas (1978).

3. Results and discussion

3.1. Structure of chloritoid

Close association of monoclinic and triclinic chloritoid with the ideal structural formula



is frequently described in the literature and specimens of chloritoid giving x-ray powder patterns characteristic of both structure types have been reported (Halferdahl 1957). The monoclinic chloritoid structure has been solved and refined (Harrison and Brindley 1957; Hanscom 1975). The triclinic structure is topologically very similar to monoclinic polymorph and the structure has been recently resolved by Hanscom (1980).

The monoclinic and triclinic chloritoid structures consist of alternating brucite and corundum-type octahedral sheets joined by isolated SiO_4 tetrahedra. Inter-layer hydrogen bonding occurs in the monoclinic structure (Hanscom 1975). Because the triclinic structure is so similar to monoclinic chloritoids, interlayer hydrogen bonding is assumed (Hanscom 1980). Halferdahl (1957) suggested that the monoclinic chloritoid structure resulted from twinning of triclinic on a unit cell scale. One possible mechanism of twinning of the triclinic structure on a unit cell scale is rotation of one unit cell relative to another (Hanscom 1980). If two triclinic chloritoid unit cells are stacked one on top of another so that their c -axes are collinear, and the upper unit cell is rotated clockwise by 60° , the resulting unit cell is very similar to that of a monoclinic polymorph.

x-ray diffraction studies have proved the existence of two monoclinic variants of chloritoid designating them as $2M_1$ and $2M_2$, in accordance with the notation used for micas. $2M_1$ is the new monoclinic structure, the cell dimensions of this variant in contrast with those of the $2M_2$ structures is that x and y axes are interchanged, with c -repeat and angle being completely different. When viewed down on (110), the $2M_2$ and $2M_1$ chloritoid structures are identical. Unit cell dimensions for the three structural types of chloritoid by x-ray diffraction methods are as follows :

A 2091

Triclinic (1Tc)	$a = 9.43 \text{ \AA}$	$\alpha = 96^\circ 03'$
	$b = 5.48 \text{ \AA}$	$\beta = 101^\circ 52'$
	$c = 9.14 \text{ \AA}$	$\gamma = 90^\circ 00'$

A 2082

Monoclinic ($2M_2 + 2M_1$)	$2M_2$	
	$a = 9.47 \text{ \AA}$	
	$b = 5.48 \text{ \AA}$	$\beta = 101^\circ 39'$
	$c = 18.14 \text{ \AA}$	
	$2M_1$	
	$a = 5.47 \text{ \AA}$	$\beta = 97^\circ 24'$
	$b = 9.47 \text{ \AA}$	
	$c = 17.90 \text{ \AA}$	

A 2092

Monoclinic $2M_2$	$a = 9.47 \text{ \AA}$	
	$b = 5.48 \text{ \AA}$	$\beta = 101^\circ 39'$
	$c = 18.14 \text{ \AA}$	

Jefferson and Thomas (1978) conclude that the $2M_1$ variant is possibly an intermediate phase in the conversion of the triclinic to monoclinic ($2M_2$) structure. In addition they have observed three layer longer period chloritoid structure in the lattice images of $2M_2$ regions of triclinic chloritoid. KB 7543 corresponds to A 2082 while HN 7801 and HN 7808 are similar to A 2092 in their cell dimensions.

3.2. Lattice images

Electron diffraction patterns of chloritoids (KB 7543) from Kibbanahalli belt (source A) had predominant streaking parallel to (001) direction indicating high disorder. Figure 1 shows a typical one-dimensional lattice image of KB 7543 wherein the $2M_1$ matrix is broken by insertion of triclinic (1Tc) intergrowths characterised by the halving of the fringe spacing. The lattice image shown in figure 2 is also from KB 7543 chloritoid, principally of the $2M_2$ matrix with intergrowths of single, triple, quadruple and quintuple layers indicating unusually high degree of disorder not observed by Jefferson and Thomas (1978) in (A 2092) monoclinic ($2M_1 + 2M_2$) chloritoid samples. In their study, lattice images of

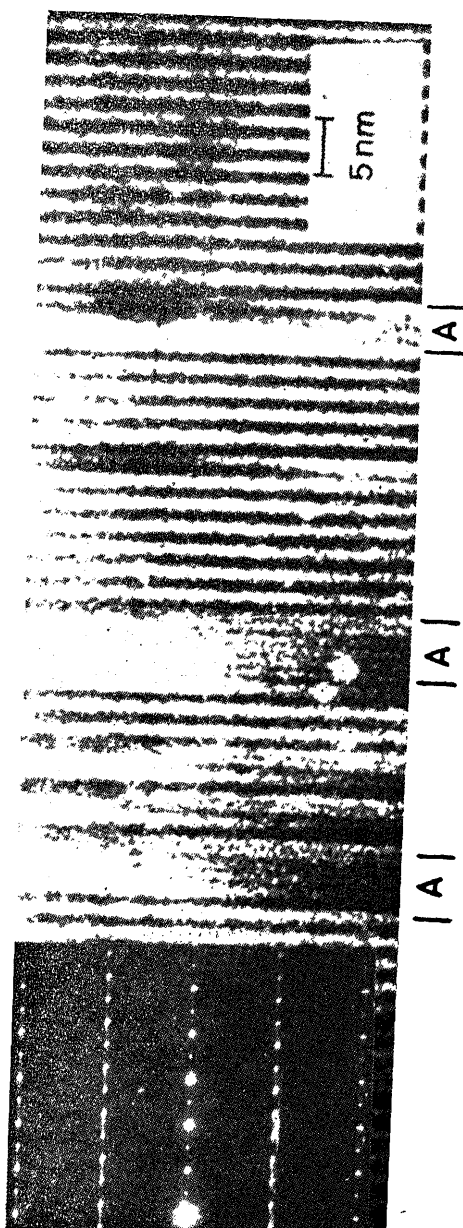


Figure 1. Lattice image of a $2M_1$ region of KB 7543 with (110) orientation. Triclinic (ITc) intergrowths are indicated as A.

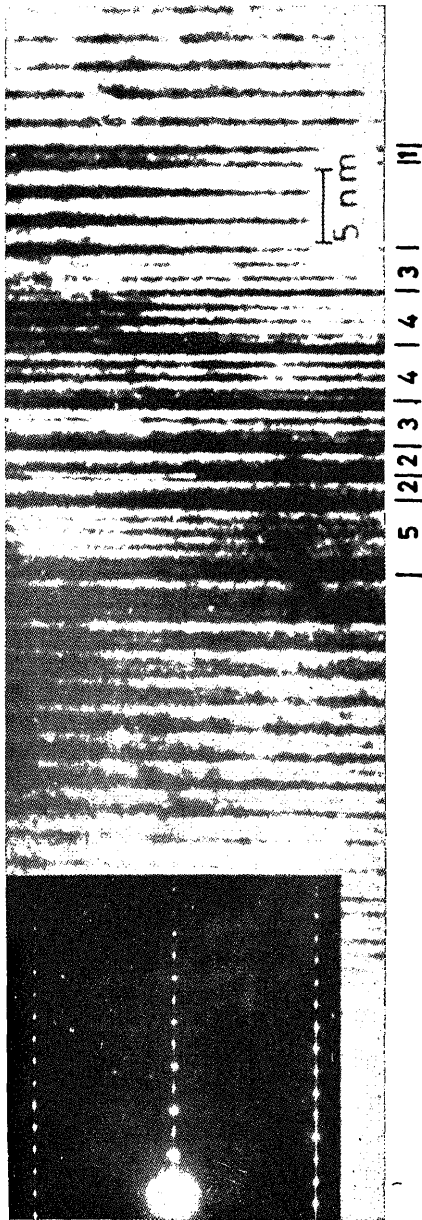


Figure 2. Lattice image of a $2M_2$ region of KB 7543 with (100) orientation. 1, 3, 4 and 5-layer intergrowths are indicated by their respective numbers.

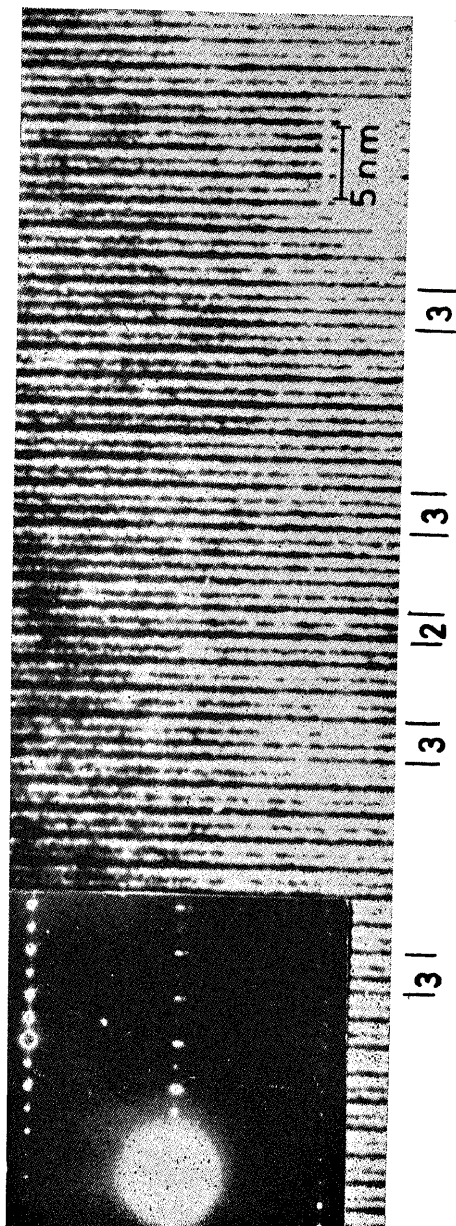


Figure 3. Lattice image of a $2M_2$ region of HN 7801 with (100) orientation. 3-layer intergrowths are indicated by numbers.

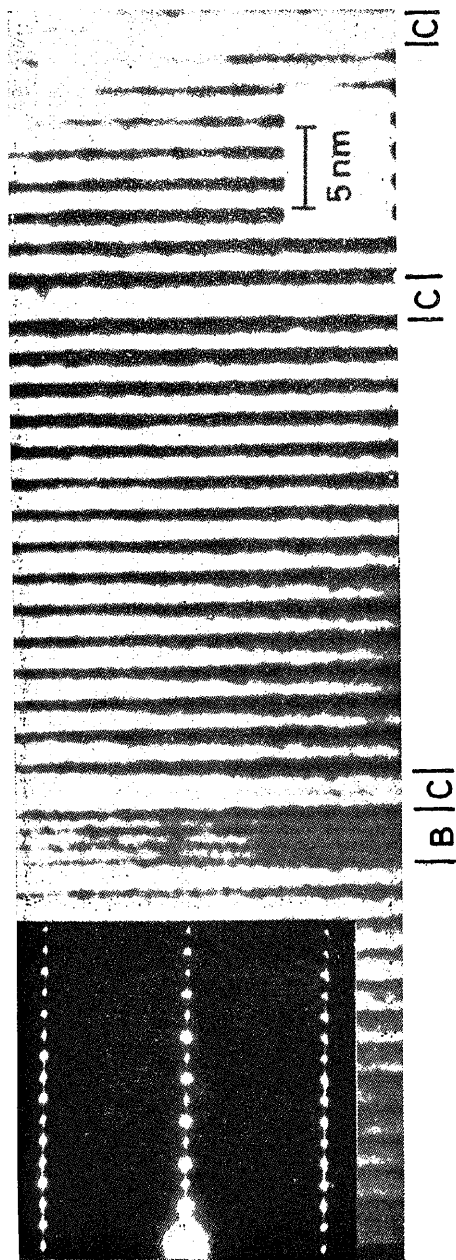


Figure 4. Lattice image of a $2M_2$ region with (100) orientation of HN 7808. Triclinic (ITc) intergrowth is indicated as B and complex intergrowths as C.

a far more homogeneous picture than the chloritoid KB 7543. This high degree of disorder, has been observed by Jefferson and Thomas only in the triclinic chloritoid (A 2091). In figure 2, two 4-layer intergrowths appear side by side flanked on either side by 3-layer intergrowths, within the $2M_2$ matrix. In addition, 1-layer and unusual 5-layer intergrowths are also present in the micrograph. The 3 and 4-layer intergrowths cannot be considered as genuine polytypes because they do not repeat three times in a sequence according to Buseck and Iijima (1974). According to Jefferson and Thomas (1978) and Jefferson (1980) the 3 and 4-layer intergrowths are genuine polytypes if they repeat twice in a sequence.

Electron diffraction patterns of HN 7801 chloritoid crystals from Holenarasipur belt (source B) indicate the principal structure to be $2M_2$ monoclinic. The lattice image shown in figure 3 is predominantly of the $2M_2$ monoclinic variant interrupted by strips of 3-layer intergrowths with rare triclinic intergrowths.

Electron diffraction patterns of HN 7808 chloritoid crystals from Holenarasipur belt (source B) showed the principle structure to be $2M_2$ monoclinic variant. The electron micrograph given in figure 4 clearly shows the true structural periodicity of $2M_2$ with triclinic (1Tc) intergrowth characterised by halving of the fringe spacing. In contrast to KB 7543, HN 7801 and HN 7808 display a far more homogeneous picture. The three layer intergrowths observed in HN 7801 were also present in some of the examined crystals of HN 7808.

3.3. *Geologic implications*

Normally triclinic chloritoid appears at the beginning of low grade metamorphism. The lower thermal stability limit for low grade metamorphism given by Winkler (1974) is 400°C . Jefferson and Thomas (1978) have observed in triclinic chloritoid a kind of unusual and severe degree of disorder. In the present work such an unusual degree of disorder is observed in the monoclinic chloritoid KB 7543. ($2M_1 + 2M_2$) variant which appears at the beginning of low grade metamorphism.

The $2M_2$ variant of chloritoid HN 7808, which displays a homogeneous picture, coexists with chlorite and almandine garnet suggests, that the stability limit of chloritoid corresponds to almandine field. Their thermal stability limit of almandine, according to Winkler (1974) is 500°C at 4 kb pressure. The thermal stability limit of the monoclinic chloritoid HN 7801 coexisting with phengite and chlorite can be inferred to be intermediate between KB 7543 and HN 7808, i.e. 450°C .

4. Conclusions

The present study of the chloritoids from different geological milieu shows that the monoclinic chloritoid KB 7543 (from source A) is a severely disordered intermediate phase in the conversion of the triclinic chloritoid to the $2M_2$ monoclinic variant. It is clear that the severely disordered $2M_1 + 2M_2$ variant marking the beginning of low grade metamorphism from Kibbanahalli belt (source A) is generated as an intermediate between a state of almost complete disorder and a completely ordered arrangement as in $2M_2$ monoclinic chloritoid, HN 7508 (from source B) coexisting with almandine garnet from Holenarasipur belt. Furthermore,

fields of the entire range of low grade metamorphism. The lattice image studies of the chloritoids indicate increase in ordered arrangement with progressive metamorphism.

Acknowledgement

The authors thank Professor C N R Rao for suggesting the problem and Dr D A Jefferson for his advice in obtaining lattice images.

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Strengths of some N-H ... π type of hydrogen bonds

G V G KRISHNA MURTY and B SUBRAHMANYAM*

Department of Chemistry, Osmania University, Hyderabad 500 007, India

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Abstract. Hydrogen bond formation between N-H of acetanilide and π electrons of some arenes has been studied by infrared spectroscopy. In the mixtures of CCl_4 and arenes new N-H bands appeared at lower frequencies in addition to the N-H band observed in pure CCl_4 . The lower frequency bands are assigned to the N-H bonded to π electrons of the arenes. Formation constants of these complexes have been determined with different arene concentrations. The frequency shifts of the N-H band and the formation constants were found to increase with increase in alkyl substitution in the benzene ring. The relative frequency shifts and logarithmic values of formation constants bear linear relationship with each other.

Keywords. N-H ... π hydrogen bonds ; formation constants ; ionisation potentials ; frequency shifts.

1. Introduction

Extensive studies were made on hydrogen bonds formed between proton donor groups and Lewis bases containing non-bonded or n -electrons (Searles and Tamres 1951 ; Pullin and Werner 1965). In the early fifties evidence was shown for the formation of hydrogen bonds with π electrons of aromatic compounds (Jones and Badger 1951 ; Tamres 1952 ; Josien and Sourisseau 1959). Infrared studies involving frequency shifts and intensity changes of the proton donor groups like hydrogen halides, OH and OD in aromatic hydrocarbons was subsequently carried out (Cook 1956 ; Basila 1961).

Association constants of the complexes between aromatics and OH were determined by Josien *et al* (1958), Basila *et al* (1965), Golinska *et al* (1968) and Yoshida Zenichi and Ishibi Nobuyuki (1969). The complexes between N-H and π electrons did not receive much attention. Josien *et al* (1958) determined the association constants of the complexes formed between N-H of pyrrole and a few aromatic compounds. Hence it was considered worthwhile to determine the association constants of N-H... π complexes using different types of N-H compounds. We report in this paper the association constants of complexes formed between acetanilide and some alkyl benzenes.

* To whom all correspondence should be made.

2. Experimental

2.1. Materials ;

Acetanilide was recrystallised twice from 200 ml of distilled water containing 4 ml of methylated spirit. The crystals were dried in an Abderhalden drier and kept in a vacuum desiccator. Benzene, toluene, xylene, mesitylene were purified by the methods suggested in the literature (Vogel 1971 ; Gilman 1932). They were kept overnight on the drying agent and distilled. The distillates were collected at the appropriate boiling points. They were again dried over sodium wire to remove last traces of moisture, and then distilled twice before use, collecting each time the middle fractions.

2.2. Measurements of spectra

As acetanilide is known to exhibit self-association in solutions of 0.01 *M* and above, the infrared spectra of this compound were recorded at 24-25° C in dilute solutions (0.002 *M* to 0.006 *M*) of CCl_4 on Perkin Elmer 337 grating spectrophotometer using matched quartz cells 0.5 cm path length. The N-H band of acetanilide was found to obey Beer's law at these concentrations (figure 1). For obtaining the free and bonded N-H bands the spectra of acetanilide were recorded in CCl_4 containing varied amounts of alkyl benzenes (0.5 *M* to 6 *M*). Solvent mixtures of the same composition were placed in the reference beam. The frequencies of free and bonded N-H stretching bands, the absorbances of the free N-H bands and the concentrations of acetanilide and alkyl benzenes are given in table 1.

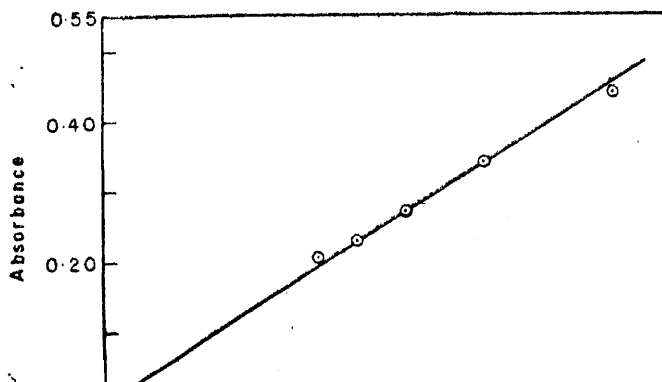


Table 1. Spectroscopic data and formation constants for the hydrogen bonding interaction between acetanilide and alkyl benzenes.

Name of the proton acceptor	Concentration of acceptor (mole lit ⁻¹)	Concentration of acetanilide (mole lit ⁻¹) $C \times 10^3$	Absorbance of free N-H (<i>a</i>)	Equilibrium constant (<i>k</i>) (lm ⁻¹)	Equilibrium constant average value	Frequency (ν) of N-H		Frequency shift $\Delta\nu$ N-H (cm ⁻¹)	Relative shift $\Delta\nu/\nu \times 10^3$
						Free (cm ⁻¹)	Bonded (cm ⁻¹)		
1. Benzene	.. 3.0870 5.1450	5.65 5.65 5.65	0.355 0.210 0.160	.. 0.22 0.24	.. 0.23	.. 3430	.. 3409	.. 21	.. 6.12
2. Toluene	2.7290 4.5460	5.65 5.65	0.200 0.145	0.28 0.32	0.30	3430	3404	26	7.58
3. <i>m</i> -xylene	.. 1.1970 1.3960	4.48 4.48 4.48	0.280 0.190 0.180	.. 0.40 0.40	0.40	3430	3397	33	9.62
4. 1,3,5-mesitylene	1.0640 1.2410	4.48 4.48	0.190 0.180	0.45 0.45	0.45	3430	3392	38	11.08
5. Hexamethyl benzene	0.5987 0.6058	4.63 3.95	0.210 0.180	0.64 0.62	0.63	3430	3385	45	13.12

* Ionization potential (IP) : Values used are of electron impact (EI) method (Basila *et al* 1965).

$$K = \frac{M_D - (a - c)/m}{[M_A - M_D + (a - c)/m] (a - c)/m}, \quad (1)$$

where M_D and M_A are the molar concentrations of the proton donor and proton acceptor respectively and a is the absorbance of the free N-H stretching band in the presence of proton acceptor, m and c are the slope and intercept of the Beer's law plot. In the present investigation the intercept c is zero. The values of K thus calculated are presented in table 1, together with the frequency shifts and the values of ionization potentials of the alkyl benzenes.

3. Results and discussion

Infrared spectrum of acetanilide in dilute CCl_4 solution exhibited only one N-H band at 3430 cm^{-1} . In the presence of alkyl benzene a new band appeared at a lower frequency the intensity of which increased with increase in concentration of alkyl benzene with simultaneous decrease in the intensity of the band at 3430 cm^{-1} (figure 2). The band at lower frequency is therefore attributed to N-H bonded to the π electrons of the aromatic hydrocarbons.

Further the frequency shift which is the difference between the frequencies of the free and bonded N-H stretching vibrations generally depends upon the dielectric constant of the solvent and local association or hydrogen bonding. Absence of linear relationship between the relative frequency shifts and $(D-1)/(2D+1)$ (figure 3) suggests that the dielectric constant of the arenes plays less significant part than hydrogen bond formation between N-H and π electrons of the alkyl benzene.

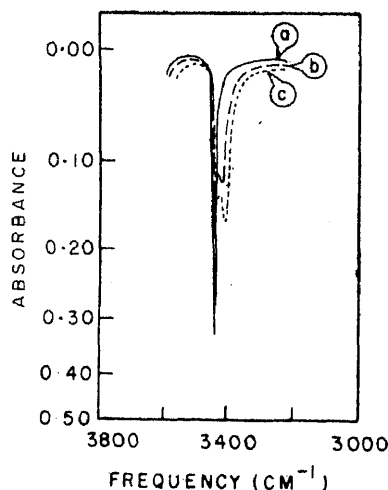


Figure 2. N-H band of acetanilide in (a) CCl_4 , (b) CCl_4 containing benzene and (c) CCl_4 containing toluene.

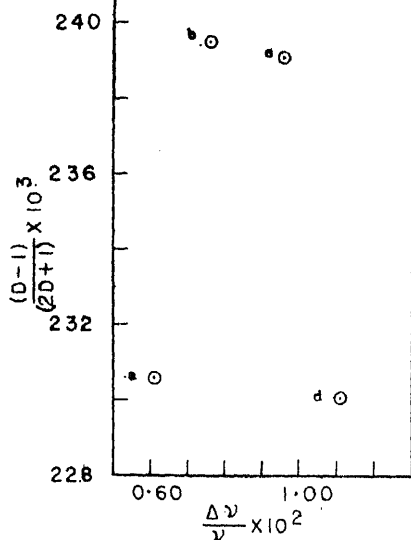


Figure 3. Plot of $\Delta\nu/\nu$ vs. $(D - 1)/(2D + 1)$: (a) benzene, (b) toluene, (c) *m*-xylene, (d) 1, 3, 5-mesitylene.

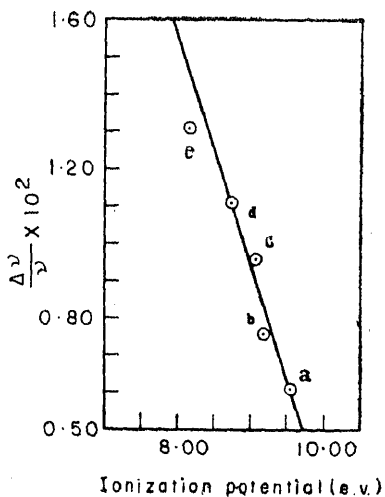


Figure 4. Plot of $\Delta\nu/\nu$ of N-H stretching band of acetanilide vs. ionisation potential of the alkyl benzene, (a) benzene, (b) toluene, (c) *m*-xylene, (d) 1, 3, 5-mesitylene, (e) hexa methyl benzene.

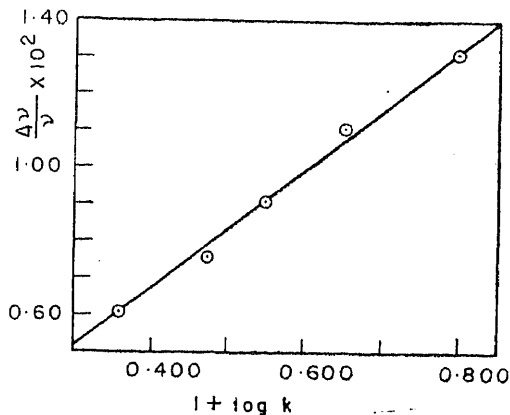


Figure 5. Plot of $\Delta\nu/\nu$ vs. $(1 + \log K)$.

The magnitude of the frequency shift is usually taken as a measure of the strength of the hydrogen bond formed (Gordy 1939 ; Gordy and Stanford 1940, 1941). The small frequency shifts observed in the present study indicate weak hydrogen bonds. Although the frequency shifts are small, they are sufficiently pronounced to distinguish among the basicities of aromatic compounds. A linear plot is observed between $\Delta\nu/\nu$ and IP of the aromatic base (figure 4). The shifts are found to increase regularly with increase in alkyl substitution in the benzene ring. Introduction of alkyl group in benzene ring decreases the IP and enhances the electron donor ability of benzene and consequently its proton accepting ability. Hence the strengths of hydrogen bonds formed with aromatic compounds studied vary in the order

hexa methyl benzene > mesitylene > *m*-xylene > toluene > benzene.

Formation constants also exhibit the same trends. There is a regular increase in the K value as the number of methyl groups in the benzene ring increases. As both frequency shifts and formation constants determine the strength of hydrogen bonds, a correlation between the two is hopefully expected. Correlation of this type fails when there are steric effects hindering the formation of hydrogen bonds because frequency shifts are presumed to depend upon the energy of the hydrogen bond whereas the formation constants depend upon energy as well as entropy. The linear plot of $\Delta\nu/\nu$ vs $(1 + \log K)$ (figure 5) shows that there are no steric effects involved to decrease the chances of hydrogen bond formation.

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Preparation and molecular configurations of some salts of dipicrylamine with organic and inorganic cations

M L KUNDU, J N KAPOOR* and S K GHOSH

Physical Research Wing, Fertilizer (Planning and Development) India Ltd.,
Sindri 828 122, India

* Chemical Research Wing

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Abstract. An investigation has been made on the structural characteristics of a class of salts of dipicrylamine with organic and inorganic cations. A general conclusion regarding the mechanism of salt formation, nature of bondings and molecular configurations of this class of salts has been suggested from the studies on infrared spectra of these salts. The main features of the spectra of all the salts are almost similar showing similar nature of bondings and molecular configurations for all the salts. In this class of salts either organic or inorganic cations are linked with dipicrylamine anion by van der Waals forces through oxygens of one of the nitro groups of the dipicrylamine. The nitro groups are twisted out of plane of the benzene rings.

Keywords. Molecular configuration; infrared spectra; cholinium salt with dipicrylamine; acetylcholinium salt with dipicrylamine; trimethylammonium salt with dipicrylamine.

1. Introduction

Dipicrylamine i.e., 2, 4, 6-2', 4', 6'-hexanitro diphenylamine is an organic analytical reagent which due to its acidic character, on treatment with sodium, ammonium, calcium and magnesium hydroxides forms corresponding soluble salts. Kertes (1956) was the first to investigate that dipicrylamine can react with organic bases like alkylamines, pyridine, piperidine etc. and studied the possibility of methods for colorimetric estimation of these organic bases. An investigation on the salt formation of dipicrylamine with organic and inorganic bases has been carried out in this laboratory and the method has been successfully utilized in the gravimetric estimation of the organic and inorganic bases in presence of common contaminants. The mechanism of salt formation and the structural details of these salts were not known. The structural characteristics of guanidinium (Ghosh *et al* 1969) and pyridinium (Kapoor *et al* 1972) salts with dipicrylamine have already been reported. In the present discourse the structural characteristics

spectrum of these salts in order to arrive at a better understanding regarding the mode of salt formation of dipicrylamine with organic and inorganic bases.

2. Experimental

2.1. Preparation of the salts

To prepare the salts, first mexan (magnesium salt with dipicrylamine) was prepared by treating a mixture of magnesium oxide and dipicrylamine in the ratio 0.416 : 1 (by weight) in a given quantity of water with constant stirring and the precipitate (mexan) thus obtained was used as reagent for other salts of dipicrylamine due to its higher solubility in water compared to that of dipicrylamine.

The cholinium, acetylcholinium and trimethylammonium salts with dipicrylamine were prepared by adding dropwise the aqueous solution of the respective chloride salts in 3% aqueous solution of mexan with constant stirring at room temperature (28-30° C). The reactions were instantaneous giving red crystalline precipitates of the cholinium, acetylcholinium and trimethylammonium salts with dipicrylamine. The precipitates were washed with ice cold distilled water and dried to constant weight at 100° C. In the case of trimethylammonium salt, the trimethylammonium chloride was first prepared by neutralizing an aqueous solution of trimethylamine (40% wt/vol) with requisite amount of *N*/10 hydrochloric acid using methyl red as indicator. The neutral aqueous solution of trimethylammonium chloride was allowed to concentrate on a water bath to obtain crystalline mass of trimethylammonium chloride.

Potassium, rubidium and cesium salts with dipicrylamine were prepared by reacting the respective chloride salts with mexan. The precipitates of the respective salts were washed with saturated solutions of the salts to make the precipitates free from mexan, if any, and dried at room temperature. The chemical composition of the products are shown in table 1.

2.2. Apparatus

2.2a. *Infrared spectra* : The infrared spectra of the salts along with the parent materials were recorded on a Perkin Elmer 421-model dual grating infrared spectrophotometer in the frequency range from 4000 to 550 cm^{-1} using a scanning speed of 17 min for the entire range. The pure and crystallised samples were subjected to infrared recording in KBr matrix. About 2 mg of the samples were mixed thoroughly with 250-300 mg KBr powder. The mixture was placed in a stainless steel vacuum die and pressed under hydraulic press for 10 min at 15 tons/sq. inch pressure. The pellets of dimension 13 mm thus formed were subjected to infrared studies.

2.2b. *Dipole moment* : The dipole moments of dipicrylamine and potassium salt with dipicrylamine were measured by the principle of heterodyne beat method in a dipole meter (WTW, Germany) with the accuracy of order 10^{-4} . Measurements were done at a frequency of 1 Mc/sec. and at 30° C in benzene solution of weight fraction not exceeding 0.05. Halverstadt-Kumlers method (Halverstadt et al 1942) was applied to calculate the dipole moment and

Table 1. Chemical composition of the resulting salts

Resulting salt	% Carbon		% Hydrogen		% Nitrogen		% Oxygen		% Metal	
	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.
ium salt with dipicrylamine $\text{Li}_4\text{NO}^+(\text{C}_{12}\text{H}_4\text{N}_7\text{O}_{12})^-$	37.67	37.65	3.47	3.35	20.40	20.66	38.30	38.35		
cholinium salt with dipicrylamine $\text{Li}_6\text{NO}_2^+(\text{C}_{12}\text{H}_4\text{N}_7\text{O}_{12})^-$	38.80	39.05	3.40	3.45	19.30	19.17	38.10	38.33		
hyl ammonium salt with dipicryl- ate $(\text{C}_2\text{H}_{10}\text{N})^+(\text{C}_{12}\text{H}_4\text{N}_7\text{O}_{12})^-$	35.95	36.15	2.85	2.83	22.60	22.49	38.40	38.53		
sium salt with dipicrylamine $(\text{C}_{12}\text{H}_4\text{N}_7\text{O}_{12})^-$	31.30	31.16	0.870	0.872	21.10	21.20	41.40	41.51	5.22	5.26
um salt with dipicrylamine $\gamma\text{-Li}_3\text{H}_4\text{N}_7\text{O}_{12})^-$	30.30	30.20	0.815	0.845	20.60	20.54	40.00	40.22	8.15	8.19
um salt with dipicrylamine $(\text{C}_{12}\text{H}_4\text{N}_7\text{O}_{12})^-$	27.48	27.52	0.765	0.770	18.85	18.72	36.55	36.66	16.28	16.32
um salt with dipicrylamine $(\text{C}_{12}\text{H}_4\text{N}_7\text{O}_{12})^-$	25.00	25.24	0.701	0.706	17.17	17.17	33.80	33.62	23.20	23.37

3. Results and discussions

The infrared spectra of all the resulting salts are almost similar. The representative spectra of one salt with organic cation (viz., cholinium salt) along with its parent materials are shown in figure 1 and the spectra of the salts with inorganic cations are shown in figure 2. The important absorption frequencies which have been affected on salt formation are listed in table 2.

The main features of infrared spectra of all the resulting salts being similar, it is expected that the nature of bonding, mode of salt formation and the molecular configurations will be same for all the salts. So, the structural characteristics with respect to cholinium salt with dipicrylamine have been discussed in detail.

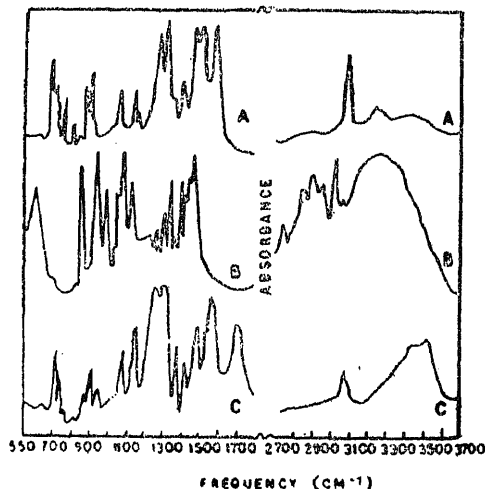


Figure 1. Infrared spectra of (A) Dipicrylamine, (B) Cholinium chloride, (C) Cholinium salt with dipicrylamine.

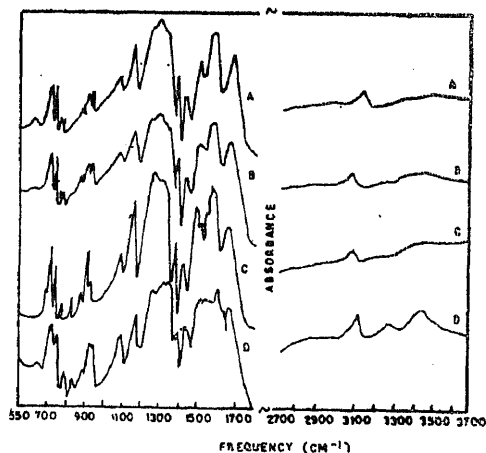


Table 2. Important absorption frequencies with assignments

Name of the compounds	Absorption frequency (cm ⁻¹) due to						
	NH stretching	Phenyl (C=C skeletal in plane)	C = N stretching (Ph—N = Ph)	C—NO ₂ asymmetrical stretching	C—NO ₂ symmetrical stretching	NH deformation in plane	CH ₃ -N asymmetrical bending
1. Dipicrylamine	3245 ms,br	1655 w,sh 1623 m,sh 1602 vs,sp		1530 vs	1345 vs	1505 m	
2. Cholinium chloride							1403
3. Acetyl cholinium chloride							1472 s 1480 vs
4. Trimethylammonium chloride							1475 vs 1401
5. Cholinium salt with dipicrylamine			1720 s	1565 vs	1333 sh		1376
6. Acetylcholinium salt with dipicrylamine			1740 s,br	1567 vs			1380
7. Trimethylammonium salt with dipicrylamine			1722 s	1562 vs	1335 sh		1473 m,sh 1378
8. Potassium salt with dipicrylamine			1665 vs	1565 s	1338 sh		
9. Rubidium salt with dipicrylamine			1665 vs	1570 s	1338 sh		
10. Cesium salt with dipicrylamine			1665 vs	1570 s	1338 sh		
11. Magnesium salt with dipicrylamine			1670 vs	1560 w	1338 sh		

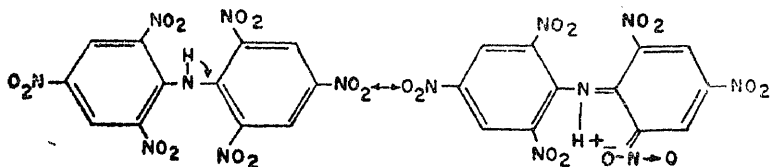


Figure 3. Resonating structures of dipicrylamine.

It may be mentioned here that dipicrylamine has a number of resonating forms of which two forms contribute predominantly to the resonance as shown in figure 3. Comparing the occurrence of absorption bands in diphenylamine and related compounds (Bellamy and Beecher 1952 ; Bellamy 1958 ; Hadzi and Skrbzlak 1957) in the region $1655\text{--}1600\text{ cm}^{-1}$, it appears that the band at $1720\text{--}1740\text{ cm}^{-1}$ region in the case of organic salts and at $1670\text{--}1665\text{ cm}^{-1}$ in the case of inorganic salts is too high in frequency to be assigned to aromatic ring vibration only. However, in the type of compounds having structural element $\text{Ph}-\text{N}=\text{Ph}$ which of course, contains $\text{C}=\text{N}$ link, a strong band at higher frequency around 1670 cm^{-1} has been observed by Marion *et al* (1951) and this is the characteristic of anilino structures, in general, and indolenines in particular. Accordingly, it is reasonable to assign the band at $1720\text{--}1740\text{ cm}^{-1}$ region to $\text{C}=\text{N}$ vibration coupled with aromatic ring vibration ($\text{Ph}-\text{N}=\text{Ph}$). This band has consistently appeared in other salts of dipicrylamine and this bonding is also in conformity with the structure of guanidinium (Gupta and Datta 1975) and potassium (Kundu and Ghosh 1980) salts with dipicrylamine determined by x-ray method. Further, the N-H deformation mode (Rud'Co *et al* 1969) which has appeared at 1505 cm^{-1} in the spectrum of dipicrylamine is absent in the spectra of the salts. These suggest that cholinium chloride reacts with resonating form (II) of the dipicrylamine in preference to that with other resonating form (I) (figure 3). This is also supported by the faster rate of reaction of cholinium chloride with dipicrylamine to form the cholinium salt with dipicrylamine. Since the reaction rate of both types of salt (organic and inorganic) is similar, it may be assumed that the band due to structural element $\text{Ph}-\text{N}=\text{Ph}$ for both types of salts appear in the region mentioned above.

The band at 1530 cm^{-1} as observed in the spectrum of dipicrylamine conforms to the normal asymmetrical $\text{C}-\text{NO}_2$ stretching vibration (Bellamy 1958). In the spectra of the salts the strong band in the region $1565\text{--}1555\text{ cm}^{-1}$ may be presumed to be the displaced frequency of the nitro groups which are twisted out of plane of the aromatic rings due to the steric effect and also due to the presence of choline ion in the vicinity of the nitro groups which take part in the salt formation by van der Waals forces. The displacement of nitro groups to higher frequency due to the presence of a strong electronegative group in the para position or of a large group in the ortho position have been stated in the literature (Conduit 1959). The same phenomenon has been observed in the structure of guanidinium salt with dipicrylamine. Similar is the case with the symmetrical vibration which has been shifted from 1345 cm^{-1} to $1338\text{--}1333\text{ cm}^{-1}$ region

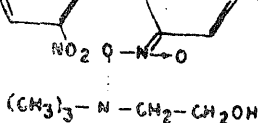


Figure 4. Possible molecular configuration of cholinium salt with dipicrylamine.

way as in the case of organic salts. In the structure of rubidium hydrogen di-*o*-nitrobenzoate and potassium hydrogen di-*p*-nitrobenzoate, Shrivastava and Speakman (1961) have shown that nitro groups are twisted out of plane of the benzene rings due to the linkage of metal ions with oxygen of NO_2 group. Banerjee *et al* (1969) have also shown that in the case of alkali metal complex with *o*-nitrobenzoic acid, $\text{N}=\text{O}$ frequency is metal sensitive. The twisting of the NO_2 groups out of plane of the aromatic rings due to the linkage like $\text{K} \cdots \text{ONO}$ is further confirmed from the crystal structure of the potassium salt with dipicrylamine. Again, the symmetrical deformation mode ($\text{CH}_3\text{-N}$) at $1410\text{-}1400\text{ cm}^{-1}$ of cholinium chloride is shifted in the salt, there is a decrease in the intensity of the asymmetrical deformation mode around 1472 cm^{-1} and enhancement of the intensity of the absorption band in the region $1380\text{-}1375\text{ cm}^{-1}$ due to the salt formation. The enhancement of intensity is probably due to overlapping of $\text{CH}_3\text{-N}$ symmetrical deformation mode in the region $1410\text{-}1400\text{ cm}^{-1}$ which has been lowered at $1380\text{-}1375\text{ cm}^{-1}$ due to the salt formation, since the absorption band at $1410\text{-}1400\text{ cm}^{-1}$ is absent in the spectra of the resulting salt. The same phenomena have been observed in the case of acetyl cholinium and trimethylammonium salts with dipicrylamine. The possible molecular configuration of the cholinium salt with dipicrylamine is as shown in figure 4.

4. Conclusion

Dipicrylamine exists in resonating forms involving structural elements, Ph-N-Ph and Ph-N=Ph which are not equivalent. When dipicrylamine reacts with organic and inorganic bases, the first resonating form is restricted and second resonating form takes part in the reaction to form the respective salts. In the structure of the salts of dipicrylamine, resonance occurs between the structures involving structural element Ph-N=Ph and Ph=N-Ph , which are equivalent. The presence of dipole moment in dipicrylamine (3.68×10^{-18} esu) and in the potassium salt (4.96×10^{-18} esu) also indicates that both structures are resonating in character which is further confirmed from the structure of the potassium salt (Kundu and Ghosh 1980). In the potassium salt the dipole moment is lowered because of less resonance energy compared to that of dipicrylamine. This suggests that the potassium salt has equivalent resonating structures while dipicrylamine has non-equivalent resonating structures (Pauling 1960).

It may therefore be concluded that dipicrylamine forms salts with both organic and inorganic cations in similar fashion. The nature of bondings and linkage

of dipicrylamine anions with organic and inorganic cations are same in both types of salts although the individual crystal structures may be different. Ghosh *et al* (1968) have shown that when potassium nitrate reacts with the guanidinium salt with dipicrylamine in water, potassium can replace guanidine ion forming the potassium salt with dipicrylamine. The exchangeability of organic ion by inorganic ion also corroborates the similar molecular configurations of both types of salts of dipicrylamine. This class of salts may be regarded as a loose molecular complex type.

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Spectral and fluorimetric studies on the effect of surfactants on thionine

S N GUHA, P N MOORTHY and K N RAO*

Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India

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Abstract. The effect of surfactants on the absorption and emission properties of thionine (TH^+) have been studied in detail. Among the various surfactants investigated sodium lauryl sulphate (SLS) has marked effect on these properties. Changes in the absorption spectrum and the decrease in fluorescence intensity at [SLS] below the critical micelle concentration (CMC) are attributed to the formation of a dye-surfactant complex. At [SLS] above CMC, the restoration of dye spectrum with increased extinction coefficient at the λ_{max} and a small but definite red shift of the λ_{max} are interpreted as due to the incorporation of the dye into the SLS micelle. The absorbance and spectral shift data suggest the thionine cation to be localized near the micelle Stern layer in the case of SLS micelles but completely outside the micelle in the aqueous environment in the case of CTABr. From the absorbance and fluorescence data, the association constant for the formation of the TH^+ -SLS complex in the premicellar region, and the binding constant for the incorporation of the dye into the micelle in the micellar region have been computed. The values of both these constants were found to increase markedly in the presence of electrolytes.

Keywords. Thionine ; dyes ; surfactants ; micelles ; critical micelle concentration ; fluorescence.

1. Introduction

The behaviour of dyes in the presence of surfactant molecules is important for understanding the thermal and light-induced reactions in biomembranes (Singhal *et al* 1970; Hevesi *et al* 1970). Such reactions occur through the mediation of excited and free radical species whose behaviour in a micellar medium can be significantly different from that in a homogeneous aqueous medium. Our main interest was the study of the photoredox reactions of the cationic dye thionine, TH^+ . Our work on this dye in homogeneous aqueous solutions has been reported earlier (Guha *et al* 1979). Before studying the photoredox chemistry in micellar systems we considered it worthwhile to study its location and interactions in such systems. We have therefore investigated the absorption and emission characteristics of this dye in the presence of various surfactants. The thionine-SLS system was studied in detail and the results are reported here.

* To whom all correspondence should be made

the red colour due to impurities disappeared in the organic phase. This was followed by twice crystallization from an aqueous HCl solution. SLS (Fluka, pract. grade) and sodium dodecyl benzene sulfonate, SDDBS (Fluka, Tech. grade) were purified by repeated washing with diethyl ether followed by drying over fused calcium chloride in a vacuum desiccator. Triton X-100 (Koch-Light, scintillation grade), Brij-35 (Pierce Chem. Co., specially purified grade) and Cetyl pyridinium chloride, CPC (E. Merck) were used as such. Cetyl trimethyl ammonium bromide, CTABr (Hopkin and Williams) was purified by dissolving the substance in the minimum quantity of methanol, precipitating with diethyl ether and drying in a vacuum desiccator over fused CaCl_2 . All other chemicals were the purest commercially available. Solutions were prepared in triply distilled water. Requisite volumes of stock solutions of thionine (10^{-3} mol dm^{-3}) and the surfactant (10^{-1} mol dm^{-3}) were diluted together to give solutions containing the two at the required concentrations. Absorption spectra were recorded on a Hitachi Perkin Elmer UV-visible spectrophotometer employing appropriate blanks, and fluorescence measurements were carried out using an Aminco-Bowman spectrofluorometer.

3. Results

3.1. Sodium lauryl sulphate

The results of both spectral and fluorescence measurements for 10^{-5} mol dm^{-3} thionine at different SLS concentrations are summarized in figure 1. Similar behaviour was observed at other dye concentrations. It is seen that with increasing SLS concentration the absorbance at 597 nm (λ_{max} of thionine) as well as fluorescence at 622 nm (for $\lambda_{\text{excitation}} = 597$ nm) both first decrease, reach a minimum at 10^{-3} mol dm^{-3} SLS, steeply rise between $1-3 \times 10^{-3}$ mol dm^{-3} SLS and level off thereafter. In the low surfactant concentration region where the absorbance of the 597 nm dye band and fluorescence intensity decrease, two new bands at 515 nm and 635 nm appear (figure 2) whose absorbances increase to a maximum at 1×10^{-3} mol dm^{-3} SLS and sharply decrease to zero in the $1-3 \times 10^{-3}$ mol dm^{-3} SLS region. Similar changes in absorption spectra and fluorescence of dyes in presence of surfactant molecules of opposite charge have been reported in the past (Corrin and Harkins 1947; Mukherjee and Mysels 1955; Malik and Chand 1972; Hevesi and Rozsa 1971). In the case of the cationic dye pinacynol and anionic surfactant SLS, a new absorption band has been observed (Mukherjee and Mysels 1955), which is not present in the pure aqueous solution. For 3,3-diethylthiacarbocyanine iodide, a cationic dye, significant change in the absorption spectrum in presence of SLS has been reported (Sato *et al* 1980). The disappearance of the dye absorption band and formation of new bands known as metachromism generally observed when the dye and surfactant bear mutually opposite charges. In the thionine-SLS (Hevesi and Rozsa 1971) and thionine-Rh6G-SLS systems (Lohoczki and Hevesi 1972) additional band at 465 nm has been assigned to a dye-surfactant complex. However, this band was observed by us only when

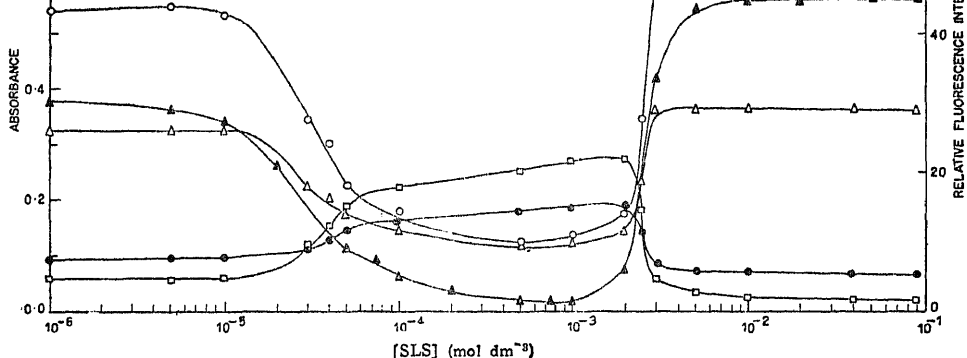


Figure 1. Effect of SLS on the absorbance and fluorescence of thionine solutions.

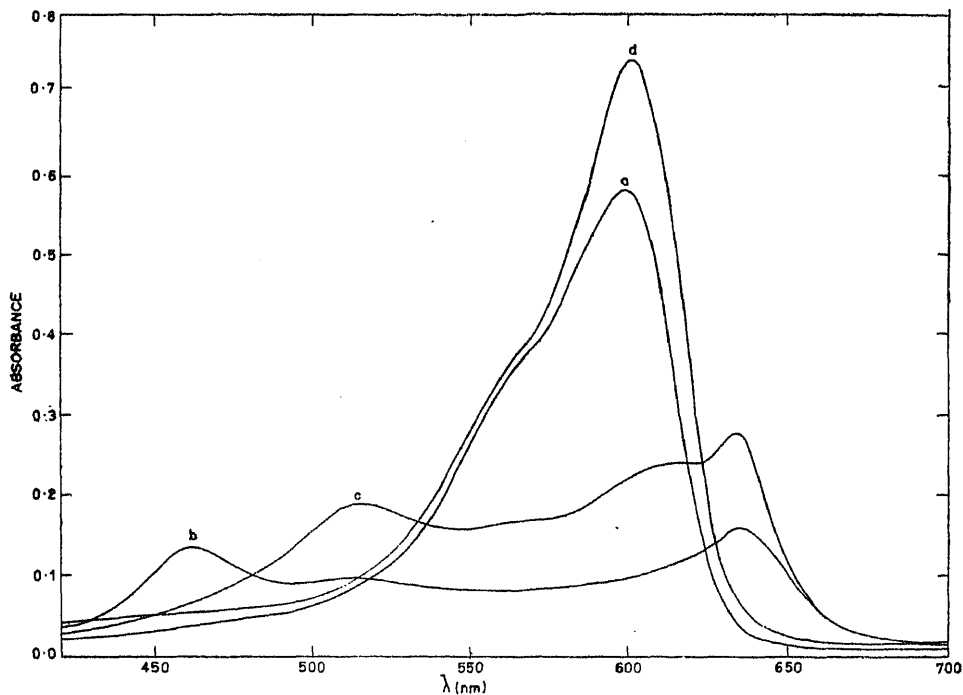


Figure 2. Absorption spectra of thionine ($10^{-5} \text{ mol dm}^{-3}$): (a) in absence of SLS; and in the presence of (b) unpurified SLS, $10^{-3} \text{ mol dm}^{-3}$, (c) purified SLS, $10^{-3} \text{ mol dm}^{-3}$, (d) purified SLS 0.09 mol dm^{-3} .

unpurified SLS was used (Curve 1, figure 2). By mass spectral analysis the impurity recovered by evaporation of the ether extract obtained during the purification of SLS was found to be dodecanol. Since the solubility of this impurity in water

bands at 515 and 635 nm. Decanol similarly added was found to show the same effect.

The colour changes observed at low surfactant concentration have been variously attributed in the past to formation of ion pairs (Colichman 1950), complexes (Malik and Chand 1972), insoluble complex salts (Klevens 1947) and dye aggregates (Corrin and Harkins 1947). The fact that such a behaviour is characteristic of oppositely charged dye and surfactant molecules agrees with the first three possibilities. Mukherjee and Mysels (1955) have in fact characterised and isolated a 1:1 dye-detergent complex salt in the case of methylene blue. In the pinacyanol-SLS system, a highly insoluble salt was found to form a stable suspension in the presence of somewhat more than stoichiometric amounts of the detergent (Mukherjee and Mysels 1955). In the present thionine-SLS system, a precipitate was observed only at $3 \times 10^{-5} \text{ mol dm}^{-3} \text{ TH}^+$ and $10^{-4} \text{ mol dm}^{-3} \text{ SLS}$. At other compositions the solutions were optically clear and precipitation could not be induced by any means. In the transition region 10^{-5} – $10^{-4} \text{ mol dm}^{-3} \text{ SLS}$ where the dye band intensity diminishes abruptly and new bands at 515 and 635 nm appear, thionine spectra were found to exhibit isobestic points at 530 and 620 nm (figure 3). Such a spectral behaviour and also the change in fluorescence intensity can be interpreted as due to an equilibrium involving association of the dye cation (D^+) and the lauryl sulfate anions (S^-):



At $[\text{TH}^+] = 5 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{SLS}] = 3.5 \times 10^{-3} \text{ mol dm}^{-3}$, Balint *et al* (1977) observed bands at 465, 515 and 635 nm in addition to the monomer band at 597 and the dimer band at 656 nm. They assigned the 465 nm band to the dye-surfactant complex and the 635 nm band to higher dye aggregates. The 515 nm band was not discussed. As mentioned before, the 465 nm band is due to interaction with the dodecanol impurity in SLS. Formation of dye aggregates in other dye-detergent systems have also been reported (Mataga and Koizumi 1954; Sato *et al* 1980). To explain the behaviour of anthraquinoid acid dyes in the presence of surfactant molecules Datyner (1961) assumed that the dye surfactant complex may aggregate to form larger particles. Except at one composition as noted above there was no precipitate formation in the thionine-SLS system and hence such aggregation of the complex to larger particles does not seem to be favoured in this system.

From figure 1 it may be seen that the disappearance of the thionine band at 597 nm and formation of the new bands at 515 and 635 nm are accompanied by decrease in thionine fluorescence. In fact at $10^{-3} \text{ mol dm}^{-3} \text{ SLS}$ when the thionine band has virtually disappeared and the absorbance at 515 and 635 nm are maximum no fluorescence is observed with λ_{ex} 515, 597 and 635 nm. Hence, it is to be concluded that the TH^+ -SLS complex is non-fluorescent. This must be due to rapid degradation of excitation energy *via* internal conversion facilitated by the long hydrocarbon chain in the SLS moiety in the complex.

Both absorbance and fluorescence data can be used to compute the association constant (K_a) between the dye cation and surfactant anion involved in equilibrium 1.

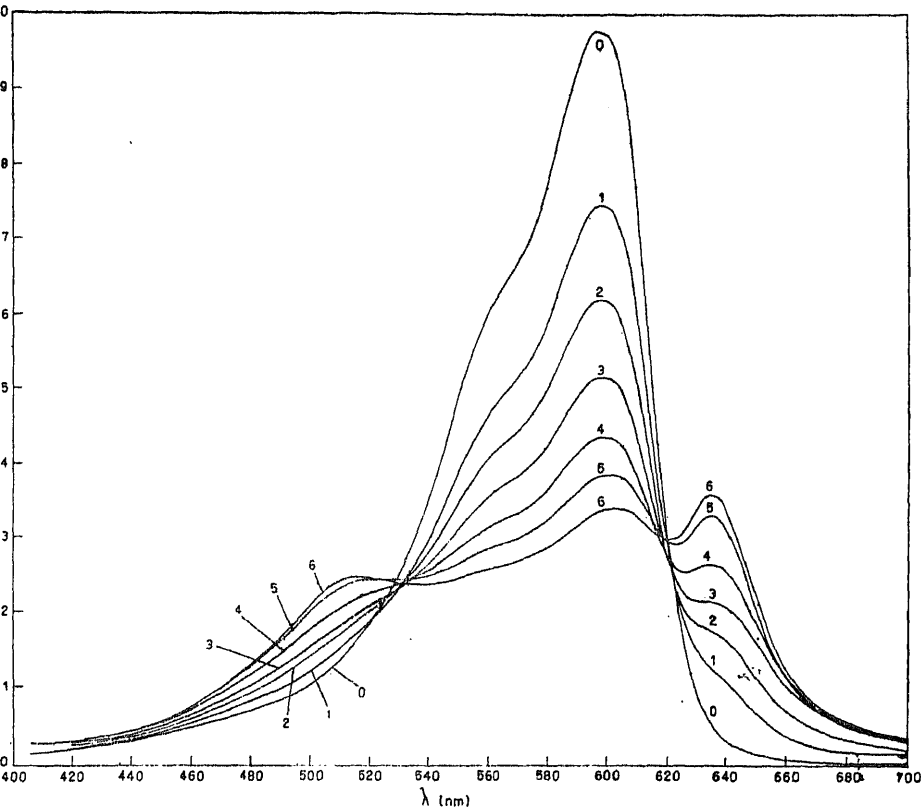


Figure 3. Absorption spectra of thionine ($3 \times 10^{-5} \text{ mol dm}^{-3}$) at different concentrations of purified SLS (0) 0, (1) 2×10^{-5} , (2) 3×10^{-5} , (3) 4×10^{-5} , (4) 5×10^{-5} , (5) 6×10^{-5} and (6) $7 \times 10^{-5} \text{ mol dm}^{-3}$.

as if the extinction coefficients of the free (or aqueous) and associated (or complexed) thionine species at a given wavelength are respectively ϵ_a and ϵ_o , the measured absorbance is given by:

$$A = \epsilon_{aq} (1 - f_o) [D]_t l + \epsilon_o f_o [D]_t l, \quad (2)$$

where f_o , the fraction of the dye present as complex is given by

$$f_o = 1 / \left\{ 1 + \frac{1}{K_a ([S]_t - f_o [D]_t)} \right\}, \quad (3)$$

the cell pathlength and $[D]_t$ and $[S]_t$ are the total thionine and surfactant concentrations. Substituting the value of f_o in (2), the measured absorbance can be shown to be related to the surfactant concentration according to:

$$\left\{ \epsilon_{aq} - \frac{A}{[D]_t l} \right\}^{-1} = (\epsilon_{aq} - \epsilon_o)^{-1} + \{ (\epsilon_{aq} - \epsilon_o) K_a ([S]_t - f_o [D]_t) \}^{-1}. \quad (4)$$

Similarly the variation in the observed fluorescence intensity I_{ob} , should follow the equation:

$$\left\{ \epsilon_{aa} - \frac{f_0}{[D]_t} \right\} \text{ vs } \{[S]_t - f_0[D]_t\}^{-1} \text{ or } 10^{-4} \text{ cm}^2/\text{l.} \text{ vs } \{[S]_t - f_0[D]_t\}$$

should be linear and K_a can be calculated from the intercept and slope of such plots. As f_0 is not known, first an approximate plot can be constructed using $[S]_t$ instead of $[S]_t - f_0[D]_t$ and the approximate K_a so evaluated then used to compute f_0 at each surfactant concentration from (3). A more accurate plot is now constructed using these f_0 values and this successive approximation procedure is repeated until the K_a and f_0 values become invariant. From the intercept of the plot corresponding to (4), ϵ_0 can be calculated as ϵ_{aa} is known. The K_a values so obtained from the measured absorbances at 597 nm and the fluorescence intensities at 622 nm agree with each other within $\pm 10\%$, the average value being $2.11 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$. K_a values were similarly computed from the absorbances at 515 nm ($2.33 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$) and 635 nm ($1.8 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$).

The extinction coefficient of the complex computed from the intercept is $0.41 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ which is about a factor of three smaller than that corresponding to the measured absorbance at $10^{-3} \text{ mol dm}^{-3}$ SLS wherein the absorbance in the 597 nm band is at a minimum. The discrepancy is attributable to an appreciable contribution from the micelle bound thionine which, as will be seen later has an extinction coefficient at 597 nm even higher than the aqueous thionine (monomeric) species.

The sharp changes in the absorbance and fluorescence occurring in the region of SLS concentration $1-3 \times 10^{-3} \text{ mol dm}^{-3}$ are related to the formation of surfactant micelles in which the dye is incorporated. Such sharp changes have in the past been made use of for the determination of the CMC of surfactants (Corrin and Harkins 1947; Mukherjee and Mysels 1955). The CMC of SLS evaluated from the inflexion points of curves in figure 4 are summarized in table 1. As observed by Mukherjee and Mysels (1955) the CMC values so obtained are lower than the ones obtained by light scattering, conductivity and viscosity measurements. Also they increase and approach the latter with increasing thionine concentration.

As mentioned before, thionine is present almost exclusively as the complex at $10^{-3} \text{ mol dm}^{-3}$ SLS and hence at this surfactant concentration the absorbance at 597 nm and fluorescence are at a minimum and the absorbances at 515 nm and 635 nm are at a maximum. Addition of electrolytes such as Na_2SO_4 , H_2SO_4 and NaCl was found to restore fluorescence and absorbance at 597 nm and bleach the 515 and 635 nm bands. Measurements made at a fixed concentration of Na_2SO_4 and varying concentrations of SLS revealed that the CMC of the latter is lowered in presence of the electrolyte (figure 4). As a result $10^{-3} \text{ mol dm}^{-3}$ of SLS is well above the CMC in presence of 0.02 mol dm^{-3} Na_2SO_4 and hence the changes observed on addition of electrolytes to a thionine solution in $10^{-3} \text{ mol dm}^{-3}$ SLS can be attributed to micellization and incorporation of the dye in the micelle (figure 5). This lowering of CMC on addition of electrolyte is in agreement with previous reports in the literature (Corrin and Harkins 1947;

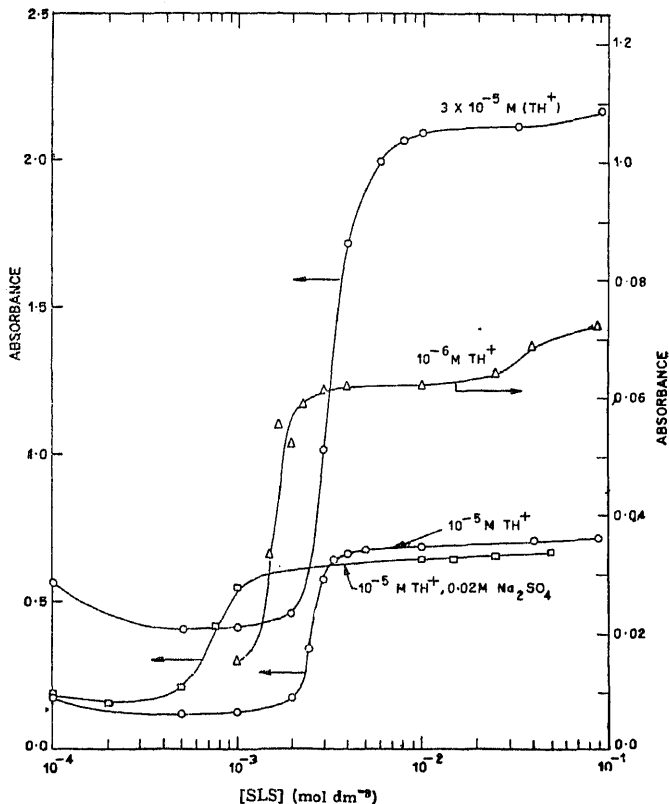


Figure 4. Dependence of absorbance (at $\lambda_{\text{max}} = 597 \text{ nm}$) on SLS concentration at different thionine concentrations and the effect of added Na_2SO_4 .

Table 1. Effect of thionine concentration on the CMC of SLS micelles.

$[\text{TH}^+] \times 10^6$ (mol dm^{-3})	CMC of SLS $\times 10^3$ (mol dm^{-3})
1.0	1.7
5.0	2.3
10.0	2.6
30.0	3.3

Muto *et al* 1973). The log-log relationship between CMC and electrolyte concentration generally observed in the case of ionic surfactants (Corrin and Harkins 1947; Schick 1964; Birdi *et al* 1980) holds good.

The restoration of the 597 nm band and the characteristic thionine fluorescence at SLS concentrations well above the CMC would indicate that the dye surfactant complex is unstable in the micellar environment. At high surfactant concentra-

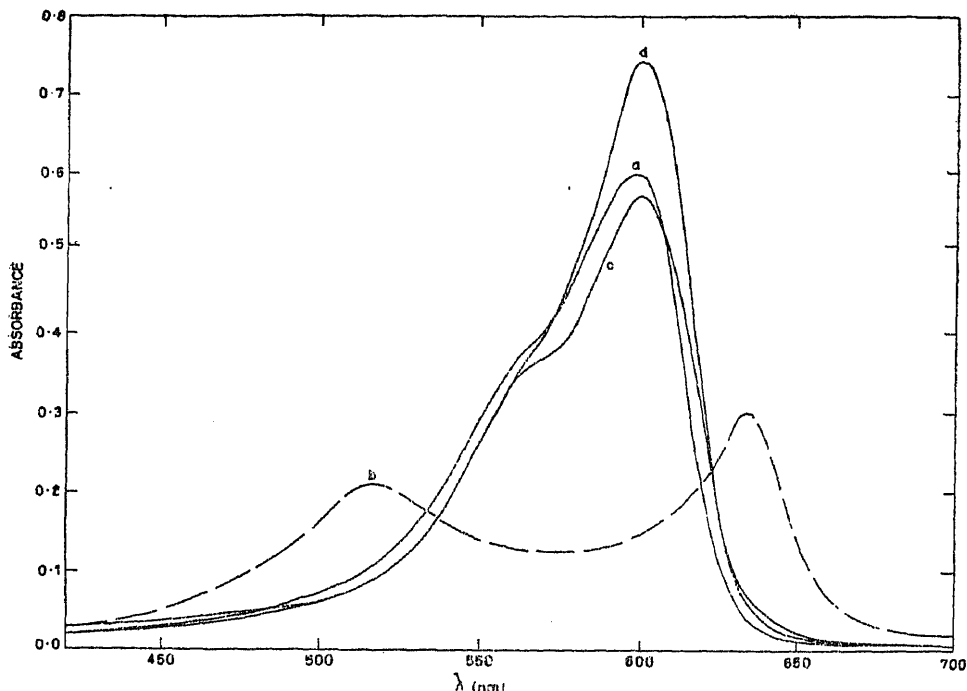


Figure 5. Effect of Na_2SO_4 on the absorption spectrum of thionine ($10^{-5} \text{ mol dm}^{-3}$) in presence of SLS (a) neat aqueous solution, (b) $10^{-3} \text{ mol dm}^{-3}$ SLS, (c) $10^{-3} \text{ mol dm}^{-3}$ SLS and 0.02 mol dm^{-3} Na_2SO_4 and (d) 0.09 mol dm^{-3} SLS.

(figure 2). Similar behaviour in other dye-detergent systems had been attributed (Kapoor and Mishra 1976) to the disaggregation of dye aggregates in the surfactant micelles to give the fluorescent monomeric species. In the thionine-SLS system, however, comparison of the absorption spectrum in the absence of surfactant and at high [SLS] revealed the presence of the dimer band in both cases although somewhat reduced in intensity in the latter (figure 2). If dye disaggregation was solely responsible for these changes then fluorescence yield after correction for reabsorption in the system should be constant, but was found to increase with increasing [SLS] above the CMC. The λ_{max} of thionine monomer band also exhibited a small but definite red shift. A more plausible explanation of the change in absorption and fluorescence in the micellar system would be that the dye in the micellar environment has a different extinction coefficient and radiative life time as compared to the pure aqueous environment. Since the dye is present as the complex in the premicellar region, the equilibrium



would be established in the micellar region, and the following equations can be derived:

where f_m is the fraction of the dye in the micellar form D^+M , and $[M]_t$ is the total micelle concentration given by

$$[M]_t = ([S]_t - \text{CMC})/\text{aggregation no.} \quad (9)$$

From the above equation it is possible, as before, to compute the dye-micelle binding constant K_b by successive approximation. The values computed from absorbance and fluorescence data agree with each other. The average value was found to be $1.37 \times 10^6 \text{ dm}^3 \text{ mol}^{-1}$. From the intercept of the plot corresponding to (7) the extinction coefficient for the micelle-bound thionine at 597 nm was found to be $6.9 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ which closely agrees with the value corresponding to the measured absorbance at the highest SLS concentration.

3.2. Effect of electrolyte addition

Both the dye-surfactant association constant K_a and the dye-micelle binding constant K_b were found to appreciably increase on addition of electrolytes such as Na_2SO_4 . The values of these constants for a few typical concentrations of Na_2SO_4 are summarized in table 2. In the region of electrolyte concentration employed, the micelle structure is not altered. In SLS, for example, the transition to rod like micelle occurs at electrolyte concentration above 0.45 mol dm^{-3} (Ikeda *et al* 1981). However, at lower electrolyte concentrations there is a small and gradual increase in micelle molecular weight and hence aggregation number. In the computation of K_b we have ignored this. The effect of this would be to give a value of K_b lower than the true value. Therefore the observed increase in binding constant with increasing concentration of electrolyte is inferred to be genuine and not an artefact of neglecting the increase in aggregation number in presence of electrolytes.

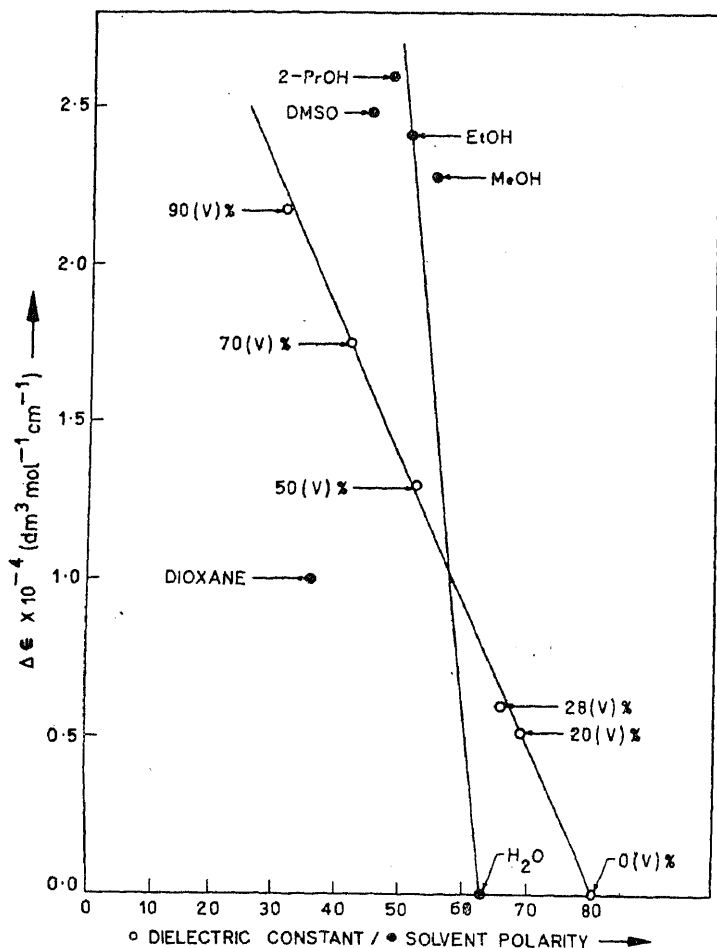
3.3. Medium polarity effects

It has been mentioned earlier that the absorbance of thionine solutions at 597 nm which reaches a minimum at $\sim 10^{-3} \text{ mol dm}^{-3}$ steeply rises near the CMC and levels off to a plateau of small positive slope beyond $3 \times 10^{-3} \text{ mol dm}^{-3}$ SLS. There is also an appreciable red shift of the λ_m , e.g., in 0.09 mol dm^{-3} SLS the maximum is shifted to 602.5 nm. At the respective maxima the extinction coefficient in 0.09 mol dm^{-3} SLS micellar medium is about 20% higher as compared to the homogeneous aqueous medium. The red shift and increase in extinction coefficient both reflect a decrease in the polarity or the dielectric constant of

Table 2. Effect of electrolyte addition on K_a and K_b values

NaCl (mol dm ⁻³)	K_a (dm ³ mol ⁻¹)	K_b (dm ³ mol ⁻¹)
NaCl	2.11×10^4	1.37×10^6
Na_2SO_4 (0.02)	4.8×10^4	7.5×10^6

the medium around the probe molecule. Thus, for example, in water-alcohol mixtures, the extinction coefficient increases linearly with decreasing dielectric constant (figure 6). From this plot the dielectric constant experienced by thionine in the SLS micellar system can be read off as ~ 56 against the observed $\Delta\epsilon_m$ of $1.1 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. Similarly, as shown in figure 6 the $\Delta\epsilon_m$ values also follow linear variations with the solvent polarity parameter, E_T (see Reichard 1965 for E_T values). Deviations from the linear correlation may be noted in the case of DMSO and dioxane. Ignoring this deviation, the polarity of the environment of thionine in the 0.09 mol dm^{-3} SLS micellar system can be inferred to correspond to an E_T value of 57.5, i.e., the polarity is between that of water and methanol. The red shift of the thionine absorption maximum also shows a correlation with the solvent polarity parameter, but as the shifts are rather small their accurate measurement is rather difficult and hence no attempt has been made to evaluate the solvent polarity parameter from this correlation.



Among the other surfactants investigated, the behaviour of thionine in the anionic surfactant SDDBS closely paralleled the behaviour in SLS: a decrease in the absorbance at 597 nm and the fluorescence intensity with increasing [SDDBS] up to $\sim 5 \times 10^{-4}$ mol dm $^{-3}$ followed by a sharp increase in the region $1 - 2 \times 10^{-3}$ mol dm $^{-3}$ culminating in a plateau beyond $\sim 3 \times 10^{-3}$ mol dm $^{-3}$. It may be noted that the CMC of SDDBS is 1.2×10^{-3} mol dm $^{-3}$. The initial decrease was accompanied by the appearance of new bands at 550 and 635 nm. As in the case of SLS the new bands disappeared at [SDDBS] > CMC. These observations are subject to the same interpretation as in the case of SLS. Association and binding constants were not calculated.

In sharp contrast to the case of SLS and SDDBS the behaviour in presence of the neutral surfactants Triton X-100 and Brij-35 and the cationic surfactants CTABr and CPC was very different. There was no decrease in the absorbance at 597 nm nor did new bands appear at surfactant concentrations below the CMC. The ion-pair type of complex is obviously not possible in the case of the cationic surfactants as thionine and surfactant head groups bear like charges. Although the neutral surfactant Triton X-100 is known to form charge transfer complex with strong electron acceptors such as TCNQ (Muto *et al* 1970) thionine seems to be too poor an electron acceptor to form such a complex with the rather poor electron donors, viz., Triton X-100 and Brij-35. Beyond the CMC there was a small but definite red shift of the thionine absorption maximum and also an increase in ϵ_m . These data together with the inferred values for the dielectric constants and solvent polarity parameters as deduced from the linear plots of figure 6 are given in table 3.

4. Discussion

Several publications have appeared on the study of micelles ever since Mc. Bain suggested aggregation of surfactant molecules above a critical concentration and Hartley's (1935) model of micelle as a tiny oil droplet in an ionic coat of hydrated ions. However many aspects of micelles pertaining to micelle shape,

Table 3. Solvent polarity and dielectric constant of different surfactant micelles as probed by TH.

Surfactant (well above CMC)	$\Delta\epsilon$	SP	DC
SLS (+0.8 M NaCl)	1.5×10^4	56.0	47.0
SLS	1.1×10^4	57.5	56.0
SDDBS	1.65×10^4	58.0	56.0
Triton X-100	1.0×10^4	58.5	57.0
Brij-35	0.6×10^4	60.5	67.0
CPC	0.4×10^4	61.5	71.5
CTABr	0.2×10^4	62.5	76.0

water penetration, surface roughness, adsorption sites, interior viscosity and chain conformation are not yet fully understood (Menger 1979). The main point of controversy in the recent past, with which of course the other questions above are to some extent tied up, is water penetration into micelles (See Wennerström and Lindman 1979 and Menger and Bonicamp 1981 for two divergent viewpoints). Whereas one extreme, the "reef" model views the micelle interior as completely dry with all the surfactant methylene groups lying entirely within the ionic coat, the opposite extreme, the "Fjord" model allows water percolation nearly to the micelle centre. Experimental results on micelles are often interpreted as evidence to support either of these extreme view points or some median view-point. Such evidences are invariably deduced on the basis of certain preconceived notions, notable among them being (i) the micelle is a closed entity (Franses *et al* 1981) with an impervious (but imaginary) boundary separating the lipophilic moieties in the interior from the hydrophilic head groups on the exterior and (ii) a solubilizate used as a probe molecule is localized in the lipophilic interior and does not perturb the micelle structure. As pointed out by both Menger (1979) and Lindman and Wennerström (1981) such questionable conclusions are due to the methodology employed in experiments designed to probe the micelle interior. In this one compares the spectroscopic properties of probe molecules in the micelle and different solvents or solvent mixtures and presupposes a correlation between such properties and the polarity of the environment indicated in terms of the dielectric constant or some empirical solvent polarity parameter. Although such correlations do exist (figure 6) what is in doubt is whether any solvent or solvent mixture can be assumed to simulate a micellar environment. Also, as is evident from figure 6, beyond a certain polarity, the measured spectroscopic parameter may exhibit an opposite trend.

In connection with this controversy regarding water penetration into micelles may be mentioned a recent neutron scattering study (Hayter and Penfold 1981), the results of which reconcile the two extreme viewpoints by supporting the idea of 'a little water penetration' into the paraffin core due to entrainment of water by the bound counterions.

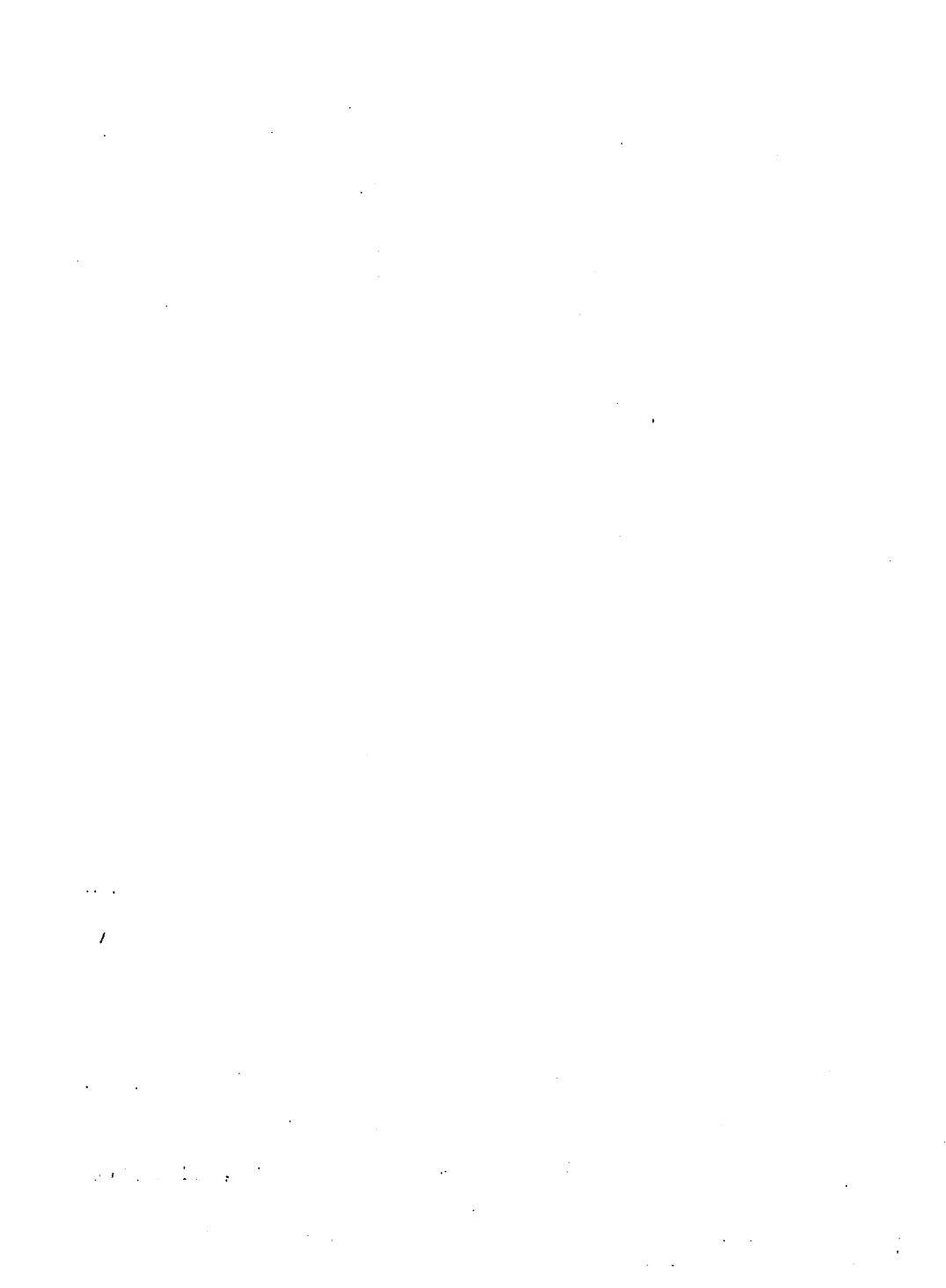
Although the question regarding the nature of micelle interior is still unresolved, there is some agreement on the location of solubilizates (Menger 1979; Lindman and Wennerström 1981). The majority of solubilizates, including the water insoluble compounds such as benzophenone, bromobenzene, pyrene, etc., prefer the highly aqueous micelle surface to the lipophilic interior. Such being the case, the location of an ionic highly water soluble compound such as thionine used in the present study should unquestionably be the highly aqueous micellar surface. In experiments employing such probe molecules, the question one has to ask is not how much water-like the micelle interior is, but how much water-unlike the surface region is. From the data summarized in table 3 it is evident that in all cases the environment around thionine is highly polar, the polarity being somewhere between that of water and methanol. The highest polarity is observed in CTABr micelles and the least in SLS micelles. Due to electrostatic repulsion of likecharged ions of TH^+ and the headgroup in CTABr, the location of TH^+ in this micellar system is expected to be farther out than in the case of SLS micelles.

the surface region of the micelles as compared to water is accountable on the basis of the surface roughness of micelles arising from their dynamic nature, i.e., monomeric units constantly enter into and exit from micelles. On an average, there is considerable protrusion of the methylene groups into the headgroup region (Aniasson 1978). This at once rules out the picture of a micelle as a closed impervious compartment and would obviously allow for penetration of water into the micelle. The water so penetrated cannot be expected to behave entirely like bulk water, but somewhat like a less extensively hydrogen bonded structure filling the crevices between the paraffin chains.

It is known (Ikeda et al 1981) that in the presence of high concentration of electrolytes larger rodlike aggregates of surfactants are formed. In such larger aggregates one can expect more methylene protrusion per micelle. This is reflected in the lower value for the polarity around thionine in SLS micellar solutions containing 0.8 mol dm^{-3} NaCl (table 3). The gradual increase in the absorbance of thionine solutions beyond the CMC (figure 1) is also attributable to the same, as it is known that larger aggregates are favoured with increasing surfactant concentration.

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Periodic precipitation of cobalt (II) oxinate in agar gel : Effect of parasitic electrolytes on flocculation

N KANNIAH, S AMBROSE, F D GNANAM and
P RAMASAMY*

A.C. College of Technology,

Perarignar Anna University of Technology, Madras 600 025, India

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Abstract. The experimental conditions for the periodic precipitation of cobalt(II) oxinate in agar agar gel have been extensively studied. When different cobalt salts are taken over the set gel impregnated with oxine, different parasitic electrolytes are formed along with cobalt(II) oxinate. These parasitic electrolytes affect the solubility and hence the periodic precipitation of cobalt(II) oxinate. The effect of the parasitic electrolytes on the flocculation value has been studied on the basis of Shinohara's revised flocculation theory. The spacing law of Jablczynski and the time law have been experimentally verified.

Keywords. Periodic precipitation; cobalt(II) oxinate; parasitic electrolyte; flocculation value; agar gel.

1. Introduction

Periodic precipitation of many sparingly soluble substances has been reported in the literature (Stern 1967). Stern (1954) has reviewed the different theories and factors influencing the periodic precipitation. Shouji Shinohara (1970) has revised the coagulation theory of Dhar and Chatterjee (1922) to explain the periodic precipitation in a quantitative manner. We have recently reported the periodic precipitation of cobalt(II) oxinate in agar agar gel (Kanniah *et al* 1981). In this paper the influence of various parasitic electrolytes on the periodic precipitation of cobalt(II) oxinate has been discussed in detail.

2. Theory

As the outer electrolyte diffuses into the gel impregnated with the inner electrolyte, the inner one itself diffuses in the opposite direction, both obeying Fick's law of diffusion given as

$$\frac{\partial C_1}{\partial t} = D_1 \frac{\partial^2 C_1}{\partial x^2}, \quad (1)$$

* To whom all correspondence should be made,

$$\frac{\partial C_2}{\partial t} = D_2 \frac{\partial^2 C_2}{\partial x^2}, \quad (2)$$

where C_1 and C_2 are the concentrations of the outer and inner electrolytes and D and D_2 are the diffusion coefficients of the outer and inner electrolytes respectively. The reaction occurs only on the boundary which is a plane perpendicular to the axis of the tube. The outer electrolyte is on one side of the boundary and the inner on the other side. The sparingly soluble reaction product remains as a sol along with the parasitic substance at the boundary, known as 'sol front'. The advancing speed of the sol front is given by

$$v = k (D_{10}/2t)^{1/2}, \quad (3)$$

where D_{10} is the diffusion coefficient of the outer electrolyte at infinite dilution calculated using Nernst equation.

The value of k which controls the behaviour of the sol front is determined by Adair using the boundary condition as

$$D_1 \frac{\partial C_1}{\partial x} + D_2 \frac{\partial C_2}{\partial x} \Big|_{\text{boundary}} = 0. \quad (4)$$

This can be conveniently written as

$$sq \lambda_{1k} + \lambda_{2k} = 0, \quad (5)$$

where

$$q = \frac{C_{10}}{C_{20}}, \quad s = (D_{10}/D_{20})^{1/2},$$

$$C_1 = C_{10} \cdot c_1, \quad C_2 = C_{20} \cdot c_2,$$

$$\lambda_{1k} = \frac{\partial C_1}{\partial x} \Big|_{\text{boundary}},$$

$$\lambda_{2k} = \frac{\partial C_2}{\partial x} \Big|_{\text{boundary}}.$$

If we assume that the diffusion coefficients are constant, then

$$D_1 = D_{10} \text{ and } D_2 = D_{20}.$$

$$c_1 = \frac{G(k) - G(k_1)}{G(k_1)},$$

$$c_2 = \frac{G(k_2) - G(k_2 s)}{\frac{1}{2} - G(k_2 s)},$$

$$\lambda_{1k} = \frac{\exp(-k^2/2)}{\sqrt{2\pi} G(k)},$$

$$\lambda_{2k} = \frac{\exp(-k^2 s^2/2)}{\sqrt{2\pi} [\frac{1}{2} - G(k_2 s)]},$$

(6)

where

$$G(k) = \frac{1}{\sqrt{2\pi}} \int_0^k \exp(-1/2 \eta^2) d\eta.$$

$$G(k) = \frac{1}{2} \operatorname{erf}(k/\sqrt{2}),$$

since

$$\operatorname{erf}(k) = \frac{2}{\sqrt{\pi}} \int_0^k \exp(-\eta^2) d\eta.$$

Substituting in (5)

$$sq \frac{\exp(-k^2/2)}{G(k)} = \frac{\exp(-k^2 s^2/2)}{1/2 - G(ks)}, \quad (7)$$

$$sq \frac{\exp(-k^2/2)}{\operatorname{erf}(k/\sqrt{2})} = \frac{\exp(-k^2 s^2/2)}{1 - \operatorname{erf}(ks/\sqrt{2})}$$

using error function

$$= \frac{\exp(-k^2 s^2/2)}{\operatorname{erfc}(ks/\sqrt{2})}. \quad (8)$$

Equation (7) is known as Adair's equation. The front constant k is calculated for different values of q using (7).

The sol front advances by forming sol of the sparingly soluble reaction product. The substance is in a state of supersaturated solution, before the formation of sol. The concentration of this supersaturated solution just before the formation of the sol, known as the reduced concentration (C_{30}) is given by

$$C_{30} = C_{10} \frac{\exp(-k^2/2)}{\sqrt{2\pi} k G(k)}. \quad (9)$$

From the above equation it can be noted that the reduced concentration (C_{30}) is constant everywhere, though the speed of the sol front slows down gradually as it advances.

As the diffusion proceeds the concentration of the outer electrolyte varies with the distance from the largest value (C_{10}) at the gel boundary to zero at the sol front. The flocculation of the sol is caused by the ions of the outer electrolyte and the parasitic electrolyte formed during the sol formation. As the ionic concentration of the outer electrolyte reaches a value Γ which is characteristic of the sol, flocculation occurs. This characteristic value Γ can be defined from (6) as

$$\Gamma = C_{10} \left[1 - \frac{G(k_1)}{G(k)} \right], \quad (10)$$

where

$$k_1 = k/p \text{ and } p = x_{n+1}/x_n. \quad (11)$$

2.1. Flocculation value

The sol of the sparingly soluble reaction product is formed with the concomitant formation of a soluble parasitic electrolyte which produces ions on ionization. The influence of the parasitic ions depends on the valency of the outer electrolyte and the parasitic electrolyte. That is whether the outer electrolyte and the parasitic electrolyte are monovalent, divalent or trivalent in action. The flocculation

solution. To this solution, 25% ammonia solution was added drop by drop until a faint but permanent turbidity was obtained. A few drops of 2*N* acetic acid were added to produce a clear solution. The pH of this solution was adjusted to 4.25. This oxine solution was mixed with agar agar gel solution and the gel solution with oxine was made upto 300 ml with hot double distilled water. This gave 0.03 M oxine in 1% agar agar. Similarly 1% agar agar solutions containing oxine of concentrations 0.06 M and 0.05 M were prepared. 50 ml of these clear solutions were poured into a corning tube of 20 mm diameter and allowed to set. After 3 hr 10 ml of cobalt(II) sulphate solutions of 1.031, 0.859, 0.687, 0.515 and 0.344 M concentrations were carefully taken over the set gel.

The experiments were carried out with cobalt(II) chloride and cobalt(II) bromide as the outer electrolytes. In all these cases the concentrations of the outer electrolyte were 1.031, 0.859, 0.687, 0.515 and 0.344 and the concentrations of the inner electrolyte were 0.06 M, 0.05 M and 0.03 M. The experiments were carried out at room temperature (30°C). Sharp brown coloured disc like precipitate rings demarcated by clear void spaces were obtained (figure 1). The distance measurements were made with a cathetometer. The IBM 1130 computer was used for the calculation of flocculation values using Shinohara's revised coagulation theory.

4. Results

4.1. Verification of time law

According to Shinohara the movement of the sol front can be expressed as

$$x_n = k (2D_{10} t)^{1/2},$$

$$\text{or} \quad \frac{x_n}{\sqrt{t_n}} = k \sqrt{2D_{10}} = K.$$

K is known as the velocity constant. For a given pair of concentrations of the inner and outer electrolytes, K is found to be a constant, thus verifying the time law. The velocity constant increases with the increase in the concentration of the outer electrolyte. Figure 2 shows the dependence of K on the concentrations of CoSO_4 , CoCl_2 and CoBr_2 , for the same inner electrolyte concentration.

4.2. Verification of the spacing law

According to Jableczynski's (1923) spacing law

$$x_n = x_0 p^n,$$

$$p = \frac{x_{n+1}}{x_n}$$

where p is known as the spacing coefficient, x_{n+1} and x_n are the positions of the $(n+1)$ th and n th rings from the gel boundary and x_0 is a constant. Figure 3 shows a plot of the numerical order of the ring (n) against $\log x_n$ for the same

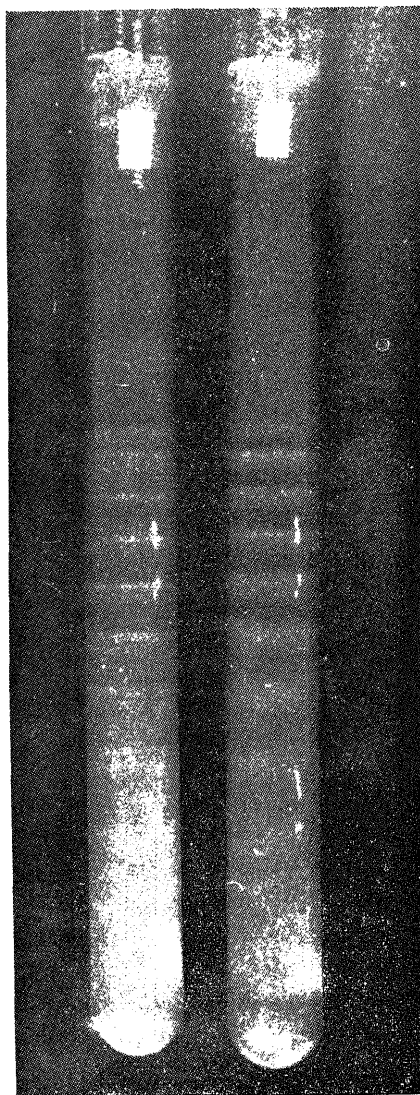


Figure 1. Periodic precipitation of cobalt(II) oxinate in agar agar gel. The concentration of oxine is 0.05 mole/litre. The concentration of cobalt sulphate is 1.031 mole/litre and 0.515 mole/litre for tubes 1 and 2 respectively.

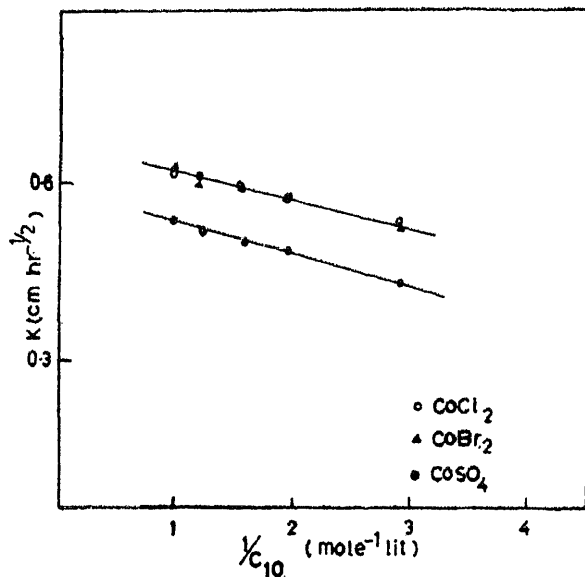


Figure 2. The dependence of K on the concentration of the outer electrolytes.

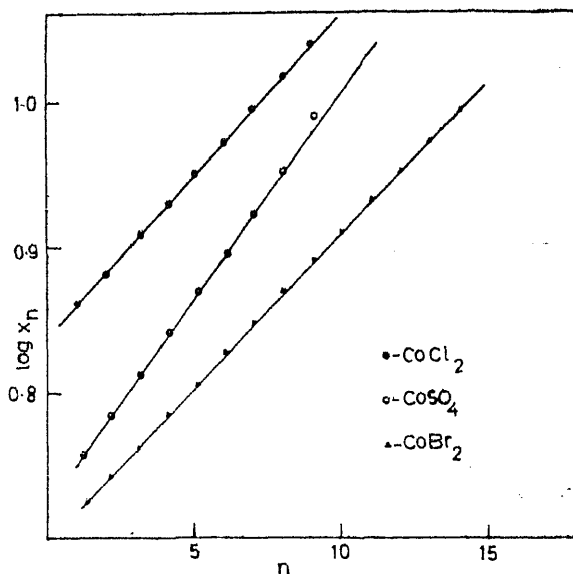


Figure 3. Verification of Jablczynski's spacing law.

concentration of the different outer electrolytes. The linear variation verifies the spacing law of Jablczynski.

4.3. *The dependence of spacing coefficient on the concentrations of the outer electrolytes*

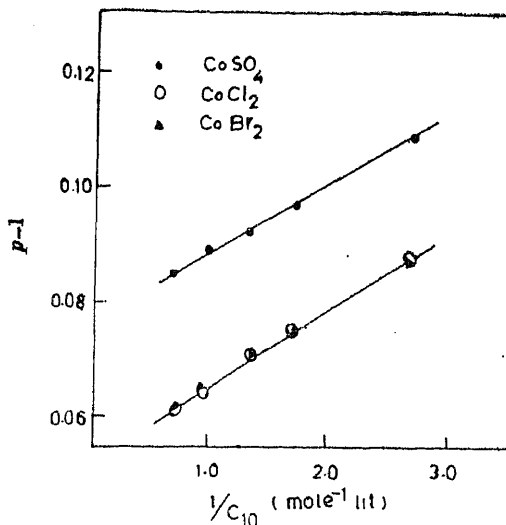


Figure 4. The dependence of spacing coefficient on the outer electrolyte concentration.

observation is true for all the outer electrolytes taken over the set gel. The dependence of the spacing coefficient on the outer electrolyte concentration has been represented in figure 4.

4.4. Calculation of flocculation value

The reduced concentration of the sol is calculated using the equation,

$$C_{30} = C_{10} \frac{\exp(-k^2/2)}{\sqrt{2\pi} k G(k)}.$$

The characteristic concentration of the outer electrolyte, Γ required to initiate flocculation is calculated using the equation

$$\Gamma = C_{10} \frac{G(k) - G(k_1)}{G(k)}.$$

Then the flocculation value of the sol

$$F = C_{30} \div \Gamma.$$

The flocculation values are computed for various concentrations of the different outer electrolytes. Table 1 shows the computed values of C_{30} , Γ , F and $G(k)$, when CoSO_4 is used as the outer electrolyte. Tables 2 and 3 show the corresponding values for cobalt chloride and cobalt bromide respectively. The computed flocculation value is the highest when cobalt sulphate is used as the outer electrolyte. The concentration of the inner electrolyte being constant, the flocculation values of cobalt(II) chloride and cobalt(II) bromide are almost equal for a particular concentration of the outer electrolyte. As the concentration of the outer electrolyte decreases, Γ value decreases for all the three outer electrolytes.

Table 1. Estimated values of C_{30} , k , Γ and F : $\text{CoSO}_4 + 2\text{C}_6\text{H}_5\text{ON} \rightarrow \text{Co}(\text{C}_6\text{H}_5\text{ON})_2 + \text{H}_2\text{SO}_4$, $s = 0.9673$.

Given t	C_{20} mole/lit	Observed		$x/\sqrt{t}$ cm hr ^{-1/2}	k	G(k)	k ₁	Estimated		F/C ₂₀	
		$q = C_{10}/C_{20}$	p					$\Gamma \times 10^2$ mole/lit	$C_{30} \times 10^2$ mole/lit		
	0.06	17.183	1.085	0.473	1.913	0.472	1.763	2.419	7.304	9.723	162.1
	0.06	14.317	1.090	0.468	1.837	0.467	1.685	2.372	7.390	9.762	162.7
	0.06	11.450	1.092	0.454	1.743	0.460	1.596	2.180	7.492	9.672	161.2
	0.06	8.583	1.097	0.409	1.618	0.447	1.475	1.990	7.667	9.657	161.0
	0.06	5.733	1.110	0.380	1.438	0.425	1.295	1.817	7.986	9.803	163.4
	0.05	20.620	1.066	0.512	1.987	0.477	1.864	1.666	6.031	7.697	153.9
	0.05	17.180	1.073	0.490	1.913	0.472	1.783	1.714	6.086	7.800	156.0
	0.05	13.740	1.079	0.458	1.820	0.466	1.687	1.685	6.170	7.855	157.1
	0.05	10.300	1.085	0.424	1.697	0.455	1.564	1.591	6.300	7.891	157.8
	0.05	6.880	1.095	0.397	1.520	0.436	1.388	1.446	6.524	7.970	159.4
	0.03	34.367	1.065	0.536	2.186	0.486	2.053	1.196	3.552	4.748	158.3
	0.03	28.633	1.072	0.510	2.116	0.483	1.974	1.248	3.574	4.822	160.7
	0.03	22.900	1.077	0.492	2.029	0.479	1.884	1.123	3.600	4.723	157.4
	0.03	17.167	1.081	0.480	1.913	0.472	1.770	1.144	3.648	4.793	159.7
	0.03	11.467	1.093	0.421	1.743	0.460	1.595	1.100	3.745	4.845	161.5

Table 3. Estimated values of C_{90} , k , Γ and F : $\text{CoBr}_2 + 2\text{C}_6\text{H}_5\text{ON} \rightarrow \text{Co}(\text{C}_6\text{H}_5\text{ON})_2 + 2\text{HBr}$, $s = 1.1798$.

Given	Observed	Estimated				F/C_{90}			
C_{90} mole/lit	$q = C_{10}/C_{90}$ p	$x/\sqrt{t}$ cm hr ^{-1/2}	k	$G(k)$	k_1	$\Gamma \times 10^2$ mole/lit	$C_{90} \times 10^2$ mole/lit	$F \times 10^2$ mole/lit	
0.06	17.183	1.063	1.927	0.473	1.813	1.728	7.045	8.773	146.2
0.06	14.317	1.066	1.854	0.468	1.739	1.679	7.077	8.756	145.9
0.06	11.450	1.069	1.762	0.461	1.648	1.586	7.143	8.729	145.5
0.06	8.583	1.076	1.640	0.450	1.524	1.518	7.260	8.778	146.3
0.06	5.733	1.087	1.465	0.429	1.348	1.368	7.472	8.840	147.3
0.05	20.620	1.051	1.999	0.478	1.902	1.249	5.839	7.088	141.8
0.05	17.180	1.055	1.928	0.473	1.827	1.257	5.855	7.113	142.2
0.05	13.740	1.062	1.837	0.467	1.730	1.281	5.910	7.191	143.8
0.05	10.300	1.066	1.717	0.457	1.611	1.195	5.994	7.189	143.8
0.05	6.880	1.085	1.545	0.439	1.424	1.258	6.134	7.392	147.8
0.03	34.367	1.061	2.190	0.486	2.064	1.104	3.513	4.627	154.2
0.03	28.633	1.063	2.123	0.483	1.997	1.074	3.508	4.582	152.7
0.03	22.900	1.067	2.039	0.479	1.911	1.043	3.507	4.550	151.7
0.03	17.167	1.068	1.927	0.473	1.804	0.939	3.519	4.458	148.6
0.03	11.467	1.083	1.762	0.461	1.627	0.958	3.577	4.535	151.2

5. Discussion

5.1. Dependence of the velocity constant

The diffusion coefficients of CoBr_2 ($1.2904 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$) and CoCl_2 ($1.2763 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$) are almost equal. The velocity of the sol (v) front is the same for both the outer electrolytes. Hence the values of the velocity constant do not show any appreciable difference. As the diffusion coefficient of CoSO_4 is very low ($0.8674 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$) the velocity of the sol front and hence the velocity constant are less than those for CoBr_2 and CoCl_2 .

5.2. Effect of concentration of the outer electrolyte on spacing coefficient

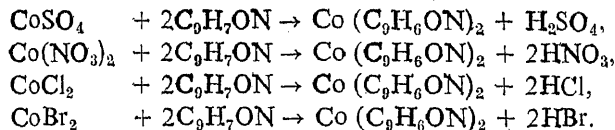
The relation between the spacing coefficient (p) and the concentration of outer electrolyte (C_{10}) is given by Matalon and Packter's (1955) equation

$$(p - 1) = A + B/C_{10},$$

where A and B are constants. The plot of $(p - 1)$ versus $1/C_{10}$ gives a straight line (figure 4). The slope of the line gives B which is directly dependent on supersaturation. Since the same straight line represents both CoCl_2 and CoBr_2 the supersaturation and the solubility of cobalt oxinate are the same when HCl and HBr are formed as the parasitic electrolytes. The slope of this line is greater than that of the straight line for CoSO_4 . This means that the degree of supersaturation is less when CoSO_4 is the outer electrolyte. In other words the presence of H_2SO_4 as the parasitic electrolyte increases the solubility of cobalt(II) oxinate.

5.3. Flocculation value

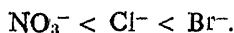
When the outer electrolyte is allowed to diffuse into the gel impregnated with oxine, cobalt oxinate is formed as a sol with the concomitant formation of a soluble parasitic electrolyte.



These parasitic electrolytes have different characteristics and produce different ions on ionization. They will have different effect on the flocculation of the positively charged cobalt oxinate sol formed due to the adsorption of excess of cobalt ion. The flocculation of the sol is caused by the counter ions supplied by the outer electrolyte and the parasitic electrolyte. So it may appear that the divalent anion—sulphate—should be more effective in flocculation than the monovalent anions, chloride and bromide. But the analysis of the tables 1, 2 and 3 shows that the flocculation value of sulphate is greater than that of others. The concentration of the supersaturated solution (C_{30}) of cobalt oxinate formed before the sol forma-

tion is greater for CoSO_4 . In other words only after the attainment of this value C_{30} , the sol formation is possible. More outer electrolyte has to diffuse to satisfy this condition. It is very clear from the foregoing arguments, that the presence of parasitic electrolyte H_2SO_4 increases the solubility of cobalt oxinate. It takes longer to exceed the solubility product. Hence the flocculation value (F) and the spacing coefficient (p) are greater than those for other outer electrolytes. This result is in accordance with Wagner's (1950) theoretical prediction. Similar results have been reported for calcite (Gnanam *et al* 1980) and silver chromate (Verma and Ghosh 1953).

We have recently reported the periodic precipitation of cobalt oxinate formed by diffusing cobalt(II) nitrate (Kanniah *et al* 1981) into agar gel containing oxine. The computed values of the concentration of the supersaturated solution (C_{30}) are identical in the case of cobalt bromide, chloride and nitrate. Hence the parasitic electrolytes HBr , HCl and HNO_3 affect the solubility of cobalt oxinate to the same extent. Until the formation of the sol the conditions are identical in the case of cobalt nitrate, chloride and bromide. However a close analysis of the flocculation values will reveal the fact that the flocculation values are in the following order :



Hence the flocculating capacity is in the reverse order.

6. Conclusion

The periodic precipitation of cobalt(II) oxinate obtained by diffusing different electrolytes into the agar agar gel impregnated with oxine reveals the influence of the parasitic electrolyte on the solubility of cobalt(II) oxinate. The flocculating capacities of different anions are compared.

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Photoelectron spectroscopic studies of the adsorption of organic molecules with lone pair orbitals on transition metal surfaces†

S YASHONATH, P K BASU, A SRINIVASAN,
M S HEGDE and C N R RAO*

Solid State and Structural Chemistry Unit, Indian Institute of Science,
Bangalore 560 012, India

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Abstract. Ultraviolet and x-ray photoelectron spectroscopy have been employed to investigate the adsorption of methanol, ethanol, diethylether, acetaldehyde, acetone, methyl acetate and methylamine on surfaces of Fe, Ni and Cu. All these molecules adsorb molecularly at low temperatures (≤ 100 K). Lone pair orbitals of these molecules are stabilized on these metal surfaces (by 0.4–1.0 eV) due to molecular chemisorption. The molecules generally undergo transformations as the temperature is raised to 120 K or above. The new species produced seems to depend on the metal surface. Some of the product species identified are methoxy species, formaldehyde and carbon monoxide in the case of methanol and methyl acetate, ethoxy species in the case of ethanol and 2-propanol in the case of acetone.

Keywords. Photoelectron spectroscopy; adsorption of organic molecules; UVPS and XPS studies of adsorption.

1. Introduction

Adsorption of molecules on metal surfaces is fruitfully studied by techniques of electron spectroscopy (Rao and Hegde 1981; Rao 1981; Thomas 1974). Ultraviolet photoelectron spectroscopy (UVPS) has been found to be specially useful in investigating electron states of adsorbed molecules and in characterizing adsorbed species (Spicer *et al* 1975; Lloyd *et al* 1977). In this laboratory, we have investigated adsorption of CO, N₂ and O₂ on transition metal surfaces by employing UVPS and related techniques (Kamath *et al* 1982a; Rao *et al* 1982; Jagannathan *et al* 1980). We considered it most worthwhile to systematically investigate the adsorption of several organic molecules possessing lone-pair orbitals on the surfaces of a few transition metals by employing UVPS. This is because such molecules would be expected to chemisorb on metals through their lone-pair orbitals and UVPS should directly give information on the nature of bonding (Luth *et al* 1977). The molecules we have examined are methanol,

† Contribution No. 166 from the Solid State and Structural Chemistry Unit.

* To whom correspondence should be made.

ethanol, diethyl-ether, acetaldehyde, acetone, methyl acetate and methylamine and the transition metals employed are Fe, Ni and Cu. It was our purpose to compare the electron states of such a related series of adsorbate molecules on the three metals and to study the thermal transformations of the adsorbate molecules. We have obtained quantitative information on the stabilization of the lone-pair orbitals of the different molecules due to chemisorption on metals by matching the experimental difference UV photoelectron spectra with the gas phase spectra (Rao *et al* 1979 ; Turner *et al* 1970) of the free molecules. We have employed x-ray photoelectron spectra in the C (1s), O (1s) and N (1s) regions to study the nature of the adsorbed species. By means of the changes observed in both UVPS and XPS, we have attempted to characterize the species resulting from the transformations of the adsorbed molecules. It has thus been possible to show that all the molecules studied adsorb molecularly at low temperatures, but undergo transformations at higher temperatures.

2. Experimental

All the spectra were recorded on the ESCA spectrometer of VG Scientific Limited, UK, fitted with a sample preparation chamber and a gas handling manifold. Specpure strips of Fe, Ni and Cu were used. The metals were etched with argon ions under UHV ($\sim 5 \times 10^{-10}$ torr) conditions to obtain atomically clean surfaces (Rao *et al* 1980 ; Jagannathan *et al* 1980). All the organic compounds were purified by fractionation. The metals were exposed to the adsorbate vapours in the sample preparation chamber to the desired extent. Exposures are referred to in Langmuirs, L ($1\text{L} = 10^{-6}$ torr sec). The temperature of the sample could be varied by using a special probe designed for the purpose. UV photoelectron spectra were recorded with HeII radiation (40.81 eV).

Difference spectra of adsorbed molecules were plotted with the aid of a DEC-1090 computer system wherein the spectra of the metals were subtracted from the observed spectra after multiplication with an appropriate attenuation factor.

3. Results and discussion

3.1. Methanol

At low temperatures (~ 80 K), methanol is found to adsorb molecularly on Fe, Ni and Cu surfaces. Thus, the HeII UV photoelectron spectra of methanol adsorbed on these metal surfaces (figures 1-3) show features very similar to those of methanol in gas phase. Difference spectra due to the adsorbed species are also compared with the gas phase spectrum in figures 1-3. The binding energy of the $6a'' + 1a'$ band in the gas phase could be matched with the third band in the difference spectra to obtain satisfactory electron states of methanol molecularly adsorbed on the three metals. The energies and assignments are summarized in table 1. We see that there is a shift of the lone-pair orbital towards higher binding energy by about 0.6 eV due to chemisorption. In x-ray photoelectron spectra

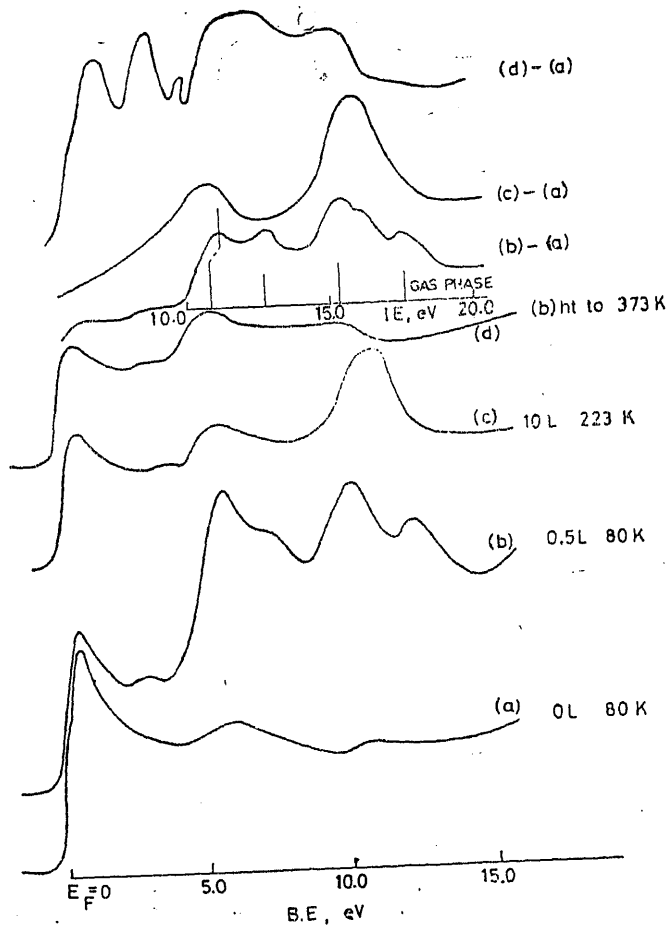


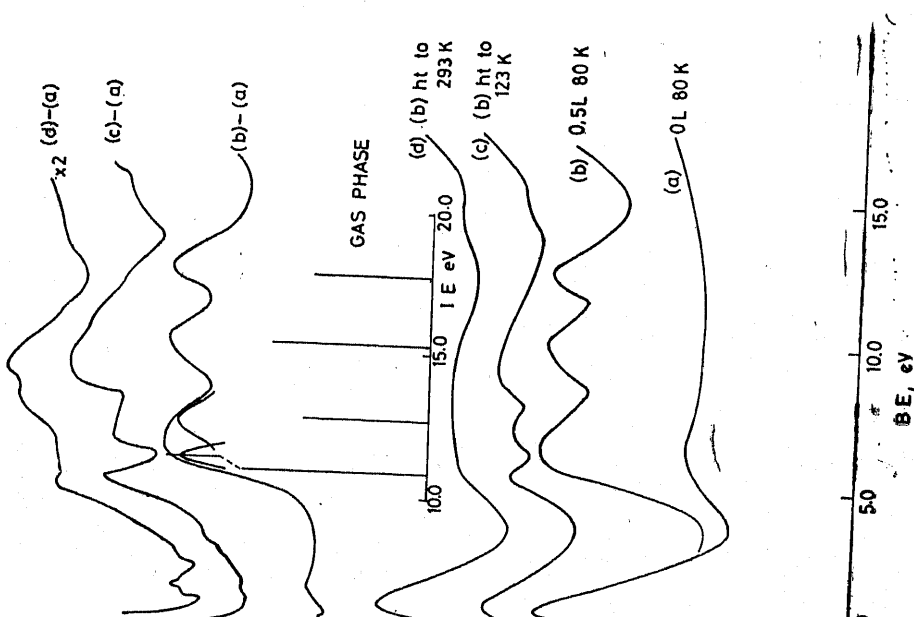
Figure 1. HeII spectra of methanol adsorbed on Fe at different temperatures and exposures. Difference spectra are also shown in the figure along with the positions of bands in the gas phase.

Significant changes occur both in the HeII spectra and the x-ray photoelectron spectra on progressively heating the sample from 80 K to 300 K. The major changes observed on the surfaces of the three metals are as follows :

3.1a. The HeII spectrum of methanol adsorbed on Fe at 223 K (figure 1) shows only two bands corresponding to $2a''$ and $6a'' + 1a'$ orbitals. The bands corresponding to $7a'$ and $5a'$ orbitals of methanol are absent in the spectrum. We attribute this to the formation of the methoxy species, CH_3O . Methoxy species is known to be formed on heating methanol on Ni surface (Kojima *et al* 1981 ; Rubloff and Demuth 1977 ; Demuth and Ibach 1979) and Cu (Bowker and Madix 1980 ; Ryberg 1981 ; Sexton *et al* 1981 ; Steinbach and Spengler 1981 ; Gault *et al* 1981). For the $C(1s)$ and $O(1s)$ bands in xps shift towards

Table 1. Electron state of molecularly adsorbed organic molecules.

Gas phase	Fe	Ni	Cu	Assignment
<i>Methanol</i>				
10.8	6.1 (0.6)	5.8 (0.6)	6.5 (0.5)	$2a'' (n_O)$
12.7	7.6	7.0	8.1	$7a' (n_O)$
15.2	10.1	9.8	10.6	$6a'' + 1a' (\sigma_{CO}; \pi_{CH_3})$
15.6	11.1			
17.7	12.4	12.3	12.8	$5a'$
<i>Diethylether</i>				
9.61	6.2 (0.8)	4.8 (0.0)	5.6 (0.0)	n_O
11.08	..	..	..	
..	8.1	7.5*	7.7*	
..	8.8			
	9.9	10.2	10.4	
16.23	12.0	11.7	12.3	
..	14.5	15.3	15.9	
<i>Acetaldehyde</i>				
10.3	5.5			$a' (n_O)$
13.24	8.0*			$a'' (\pi_{CO})$
14.15				$a' (\sigma)$
15.34				$a' (\sigma)$
15.6	10.5*			$a'' (\pi_{CH_3})$
16.47				a'
<i>Acetone</i>				
9.7	..	4.6 (0.5)	5.5 (0.4)	$a' (n_O)$
12.6	..	8.5*	9.1*	$a'' (\pi_{CO})$
14.0	..			$a'' (CH_3)$
15.7	..	10.2	11.2	$a'' (\pi_{CH_3})$
18.15	..	12.65	13.7	$a' (\pi_{CH_3})$
<i>Methyl acetate</i>				
10.5	6.4 (0.4)	5.8 (0.3)	6.5 (0.3)	n_O
11.3				$\pi_{C=O}$
12.9	8.4	7.7	8.5	
14.05	10.1	9.4	10.3	
14.9				
16.3	12.0	11.35	12.2	
	14.3	13.6	14.5	
<i>Methylamine</i>				
9.6	6.0 (1.0)	..	5.8 (0.6)	n_N
13.2	8.55	..	8.0	π_{CH_3}
14.3				



HeII spectra of methanol adsorbed on Ni at different exposures and exposures. Difference spectra are also shown in the figure along with the position of bands in the gas phase.

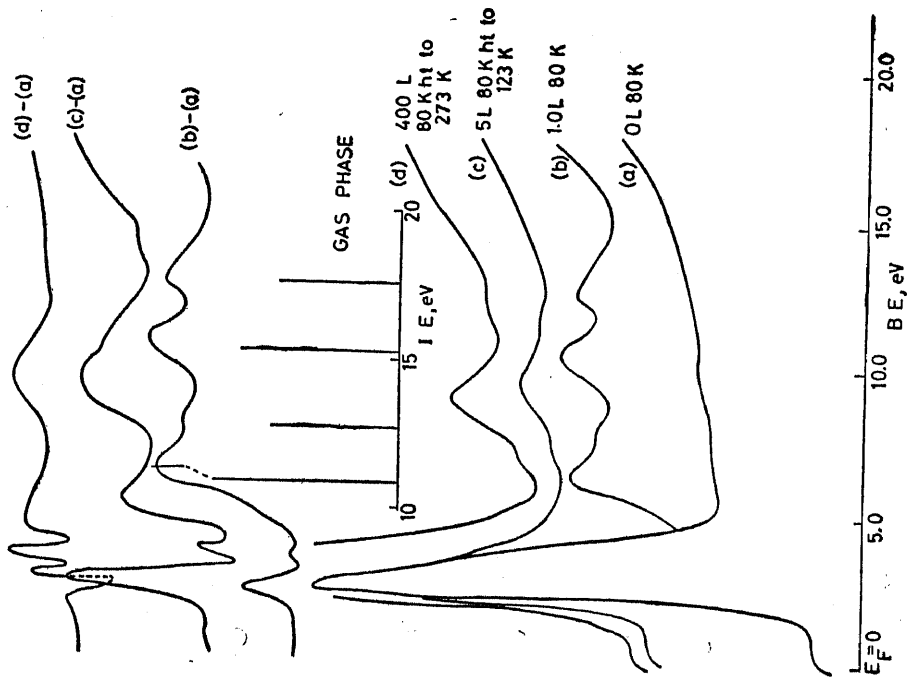


Figure 3. HeII spectra of methanol adsorbed on Cu at different temperatures and exposures. Difference spectra are also shown in the figure along with the positions of bands in the gas phase.

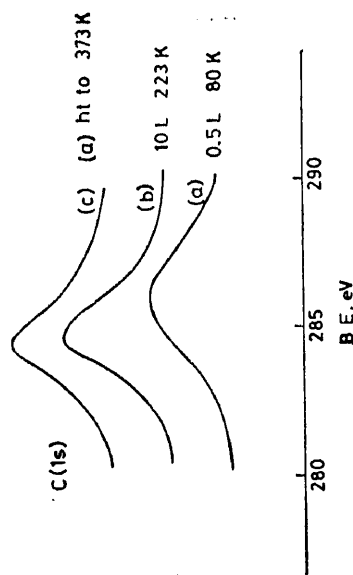
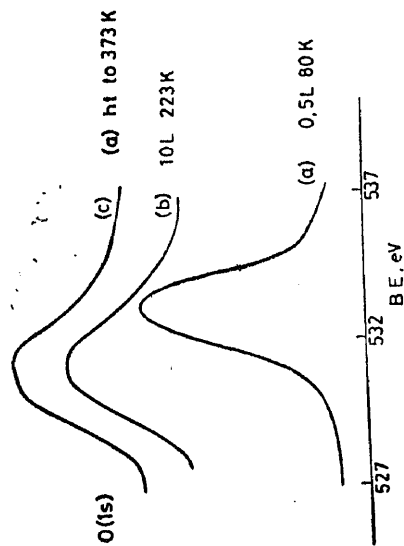


Figure 4. Carbon 1s and oxygen 1s bands in xps of methanol adsorbed on Fe at different temperatures and exposures.

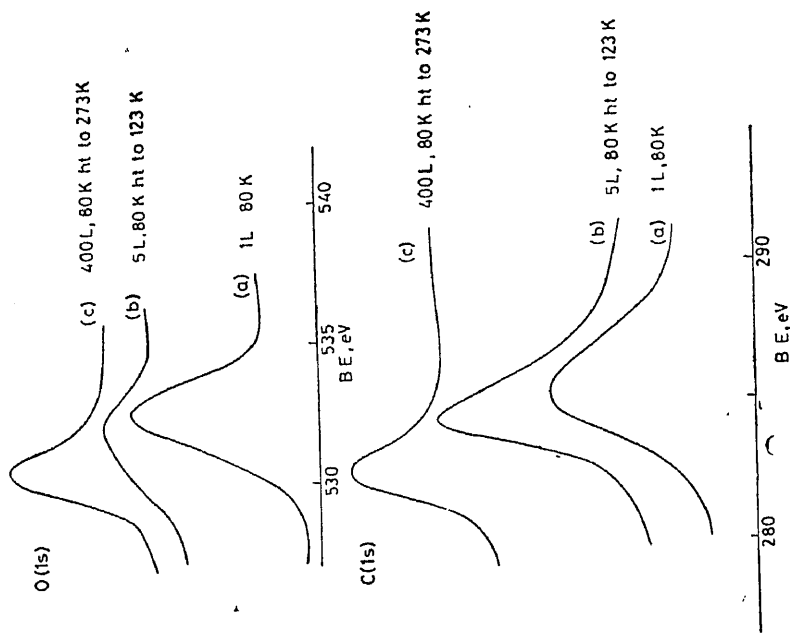


Figure 5. Carbon 1s and oxygen 1s bands in xps of methanol adsorbed on Cu at different temperatures and exposures.

3.1b : In the case of Cu, warming to 123 K results in the appearance of two bands at 5.3 and 9.3 eV in the difference spectrum (figure 3). Formaldehyde adsorbed on Cu gives a UV photoelectron spectrum (Kojima *et al* 1981) very similar to that shown in figure 3 with bands at 5.4 eV and 8.5 eV (weak) as well as a broad band extending between 8.9 and 11.0 eV with the maximum around 10 eV. The C(1s) and O(1s) bands in xps at 123 K are shifted towards lower binding energies suggesting a decomposition of methanol (figure 5). It, therefore, appears that methanol dissociates to give formaldehyde on the Cu surface studied by us at 123 K. This observation differs from that of Bowker and Madix (1980) who found the methoxy species on Cu (110) surface when methanol adsorbed at 140 K was subsequently heated to 270 K ; these workers employed much higher exposures than in the present study.

3.1c : In the case of Ni, warming to 123 K results in drastic changes in the HeII spectrum (figure 2). The C(1s) and O(1s) bands in xps are shifted towards lower binding energies indicating new species due to decomposition of methanol. We attribute the complex HeII spectra to the presence of more than one type of species, probably CH_3O , H_2CO and other products ; such products are known to be formed on Ni surface (Kojima *et al* 1981 ; Demuth and Ibach 1979).

3.1d : On warming to 300 K or higher, we observe considerable changes in the uvs of the adsorbed species on all the three metal surfaces. The C(1s) and O(1s) bands in xps are also further shifted to lower binding energies (figures 4 and 5) and appear around 284.0 eV (282.7 eV for Cu) and 530.6 eV respectively. These changes suggest the formation of CO and carbide species on the metal surfaces due to the decomposition of the intermediate species observed at 123/223 K.

Our observation of the occurrences of different types of transformations of methanol on the three metal surfaces studied by us is interesting indeed. In table 2 we show the various adsorbed species formed on Fe, Ni and Cu surfaces at different temperatures. We can understand the formation of CH_3O and H_2CO from CH_3OH on metal surfaces in terms of the sequences shown in chart 1. Thus, the formation of methoxy species on Fe surface could occur as shown in sequence (a) of chart 1. Formation of H_2CO can occur either by sequence (b) or (c) in chart 1. Sequence (c) has been noticed on Ag metal by Wachs and Madix (1978). However, in the case of Cu, sequence (b) is more probable since the heat of chemisorption of hydrogen (ΔH_a) is somewhat low. In table 3 we have listed the heats of chemisorption of hydrogen taken from Stevenson (1955). We see that on Cu, ΔH_a is lowest suggesting thereby that adsorption of hydrogen is not as favoured. Formation of H_2CO may therefore not occur by sequence (c) which would require chemisorption of hydrogen on Cu.

3.2. Ethanol

Figure 6 shows the ultraviolet photoelectron spectrum of ethanol adsorbed on Fe at 273 K. The spectrum shows four distinct bands at 5.5, 7.8, 9.2 and 10.5 eV. On comparison with the gas phase spectrum of ethanol, we see that bands due

Table 2. Products obtained from methanol, ethanol, diethylether, methyl acetate and methylamine adsorbed on metal surfaces.

Approximate temperature (K)	Fe	Ni	Cu
<i>Methanol</i>			
80	CH ₃ OH	CH ₃ OH	CH ₃ OH
123/223	CH ₃ O	Transformation products	H ₂ CO
300	CO	CO	CO
<i>Ethanol</i>			
273	C ₂ H ₅ O	..	..
<i>Diethylether</i>			
80	C ₂ H ₅ OC ₂ H ₅ (chemisorbed)	C ₂ H ₅ OC ₂ H ₅ (physisorbed)	C ₂ H ₅ OC ₂ H ₅ (physisorbed)
223-323	Transformation products	Transformation products	Transformation products
<i>Methyl acetate</i>			
80	CH ₃ COOCH ₃	CH ₃ COOCH ₃	CH ₃ COOCH ₃
123/173	CH ₃ O	Transformation products	H ₂ CO
<i>Methylamine</i>			
80	..	..	CH ₃ NH ₂
123	..	..	Partial decomposition
173	CH ₃ NH ₂ + decomposed products	..	..
300	Decomposition products	..	Decomposition products

(1981). Ethanol is apparently adsorbed molecularly only at low temperatures just as methanol.

3.3. Diethylether

Figures 7-9 show the UVP spectra of diethylether adsorbed at 80 K on Fe, Ni and Cu surfaces. Difference spectra and the gas phase spectrum are also shown in these figures. In table 1 we have shown the positions and assignments of chemisorbed diethylether. On matching the most intense band of the difference spectra with the 17.2 eV gas phase band, we find that the lone-pair orbital shows a shift of about 0.8 eV on Fe due to chemisorption ; no such shift is observed on Cu and Ni surfaces. Thus the spectra in figures 7-9 are consistent with

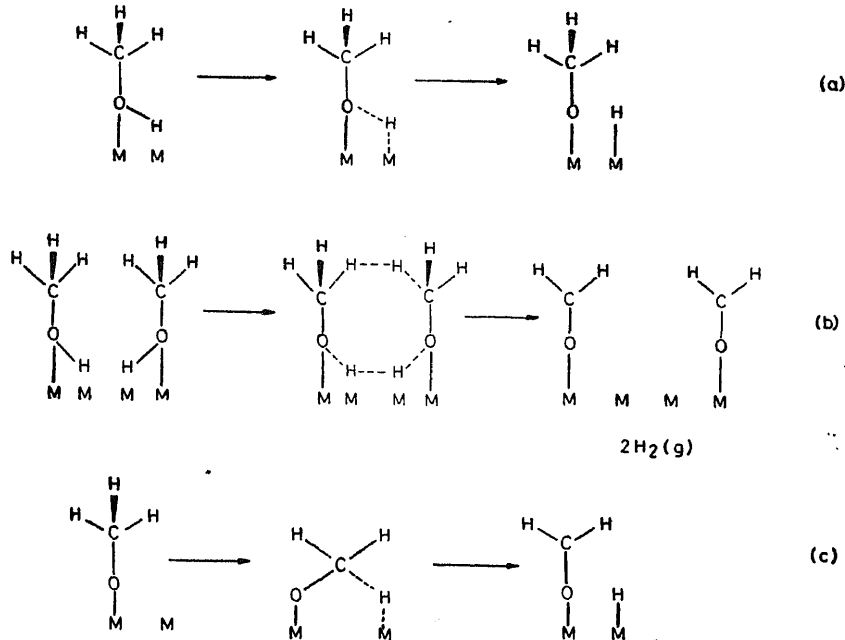


Chart 1. Mechanism of formation of methoxy species and formaldehyde from methanol adsorbed on metals.

Table 3. Heat of chemisorption of hydrogen (ΔH_a) on metals and the products formed by methanol on their surfaces.

Metal	$-\Delta H_a^*$ kcal/mole	Product on warming to 123/223 K
Fe	31.6	CH_3O
Ni	28.9	$\text{CH}_3\text{O}/\text{H}_2\text{CO}$
Cu	25.6	H_2CO

* From Stevenson (1955).

finding this difference in behaviour amongst the three metals ; errors in matching the gas phase and difference spectra could partly contribute to this difficulty since there are only three bands in the gas phase spectrum. xps spectra in the C (1s) and O (1s) regions of Fe and Ni surfaces are shown in figures 10 and 11. The C (1s) region shows two distinct bands in the case of Fe at 286.5 and 289.6 eV while in the case of Ni (and Cu, not shown in the figure) a single band at 285.9 is observed. The O (1s) band appears around 533.7 eV. xps and uvps data suggest that molecular diethylether interacts in a distinctly different way with Fe as compared to Ni and Cu.

On warming, drastic changes are observed in the uvps spectra (figures 7-9)

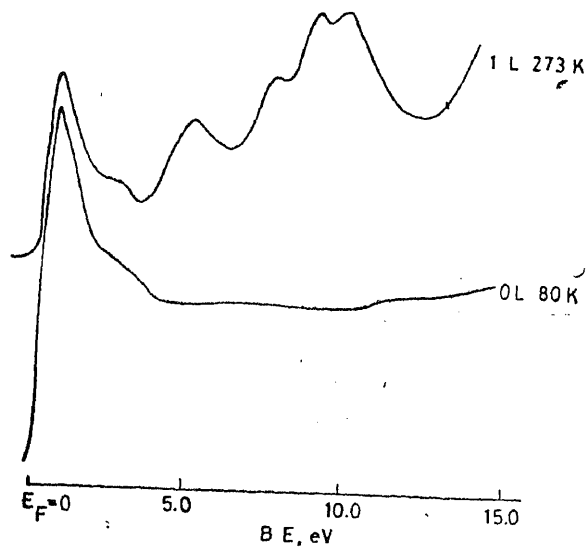


Figure 6. HeII spectra of ethanol adsorbed on Fe at 273 K.

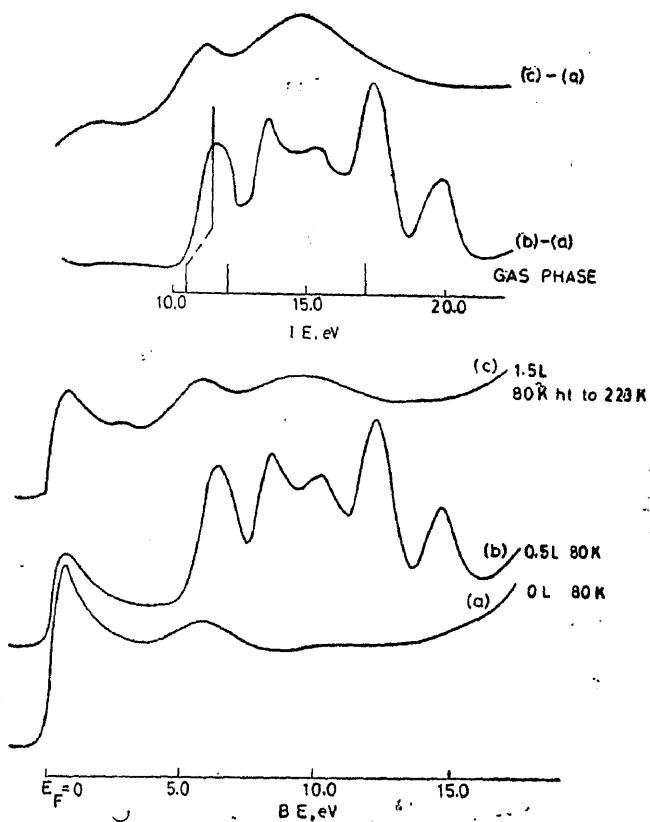


Figure 7. HeII

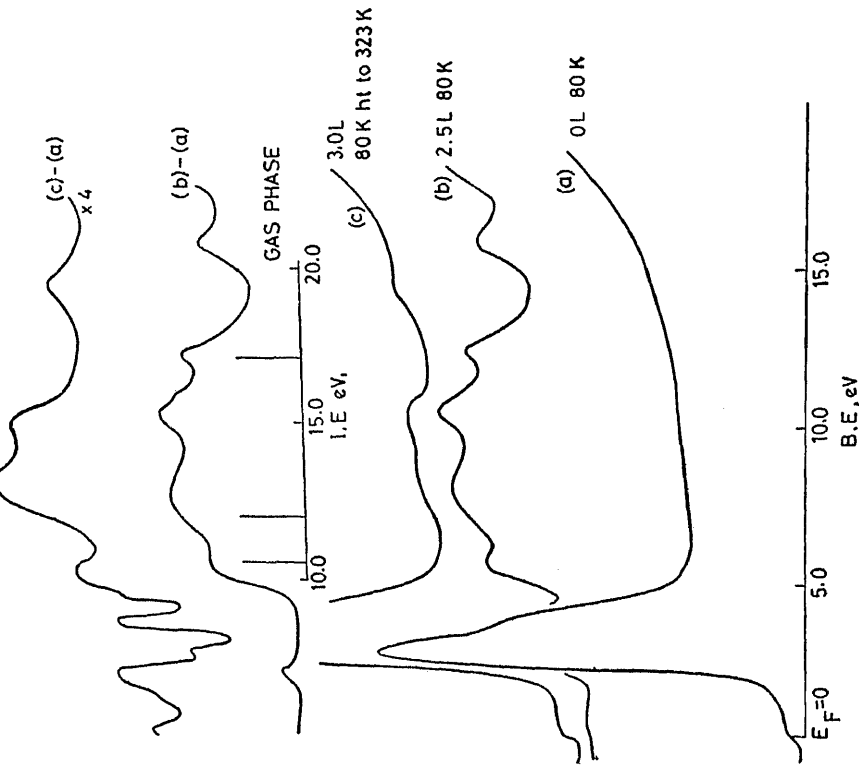


Figure 9. HeII spectra of diethyl ether adsorbed on Cu at different temperatures and exposures. Difference spectra are also shown along with the positions of bands in the gas phase.

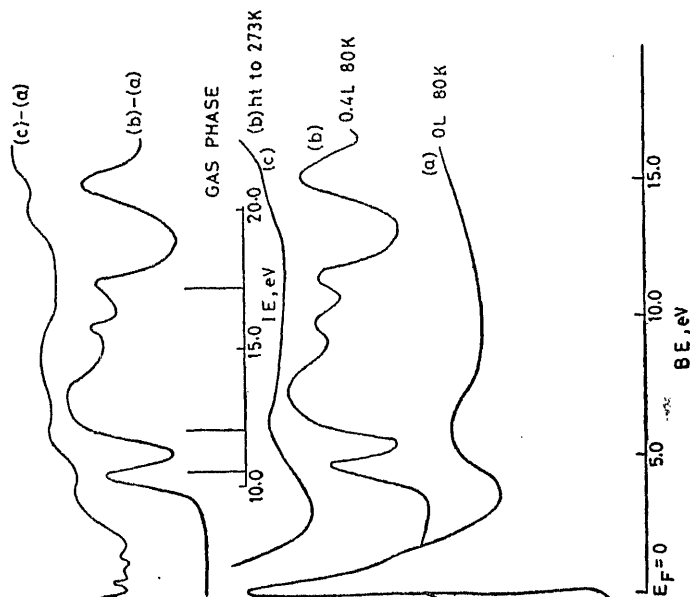


Figure 8. HeII spectra of diethyl ether adsorbed on Ni at different temperatures and exposures. Difference spectra are also shown along with the positions of bands in the gas phase.

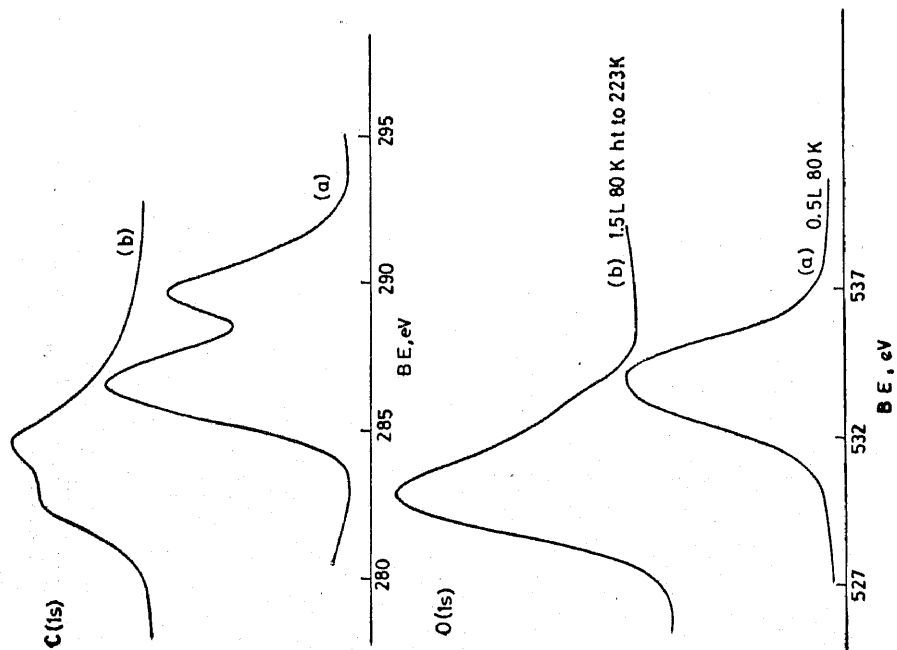


Figure 10. Carbon $1s$ and oxygen $1s$ bands in xps of diethyl ether adsorbed on Fe at different temperatures and exposures.

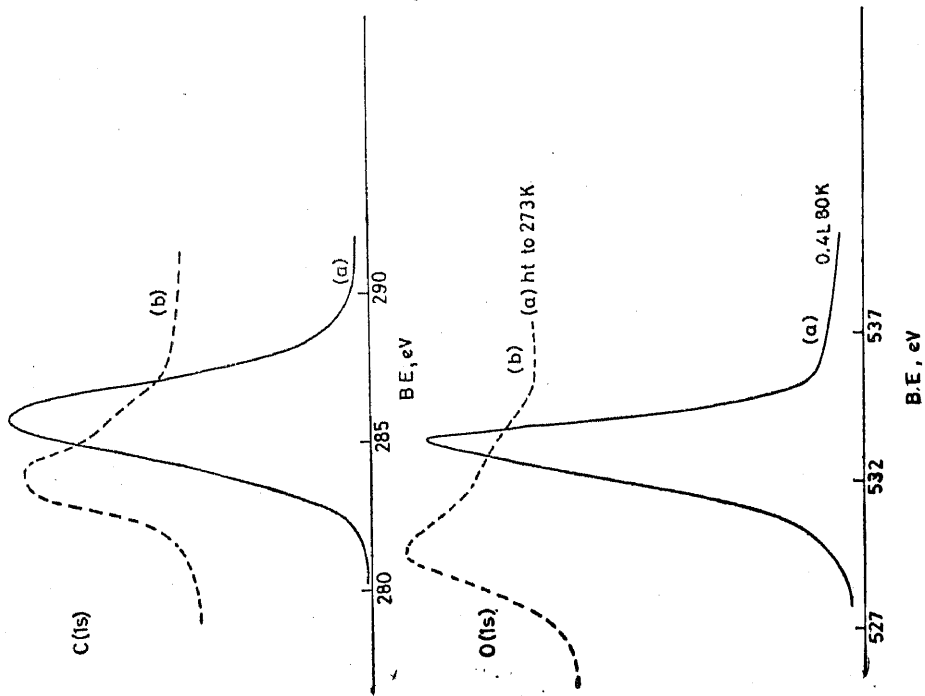


Figure 11. Carbon $1s$ and oxygen $1s$ bands in xps of diethyl ether adsorbed on Ni at different temperatures and exposures.

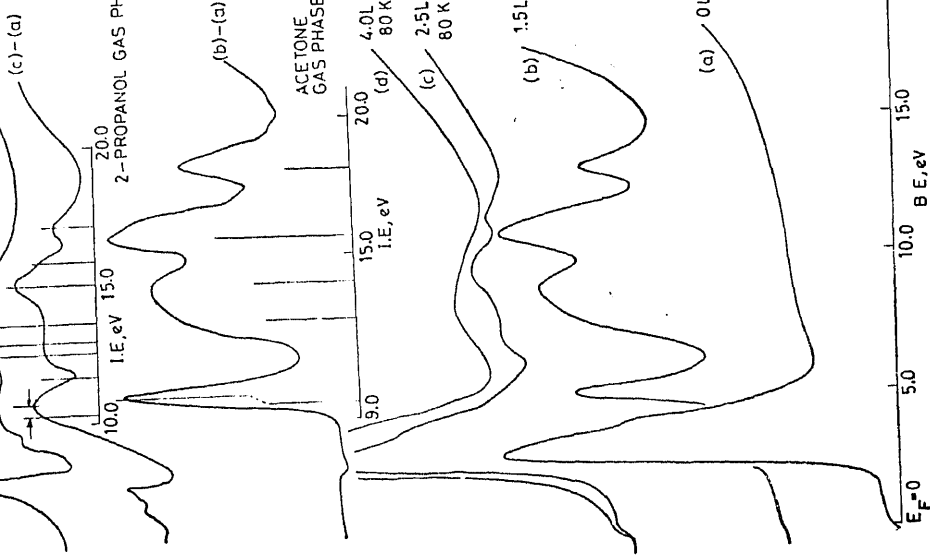


Figure 12. HeII spectra of acetone adsorbed on Ni at different temperatures and exposures. Difference spectra are also shown along with the positions of bands in the gas phase.

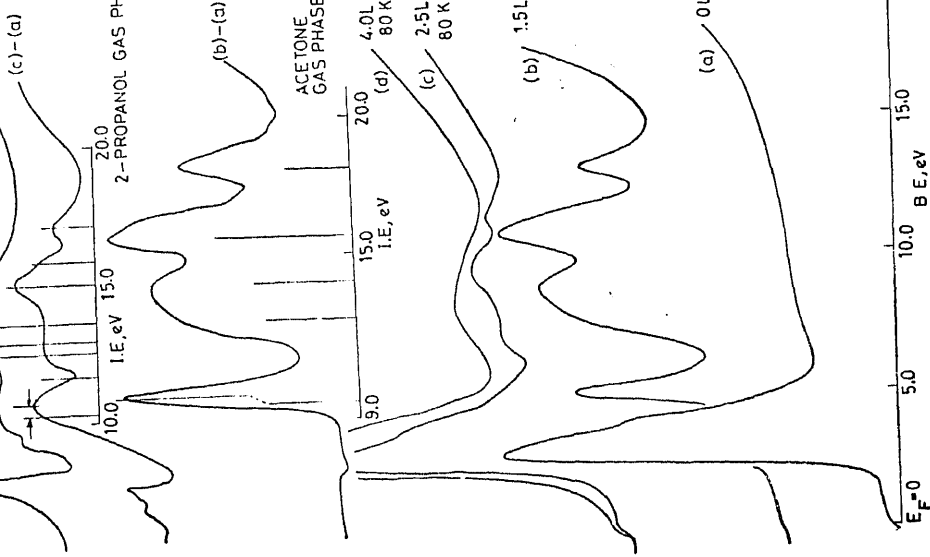
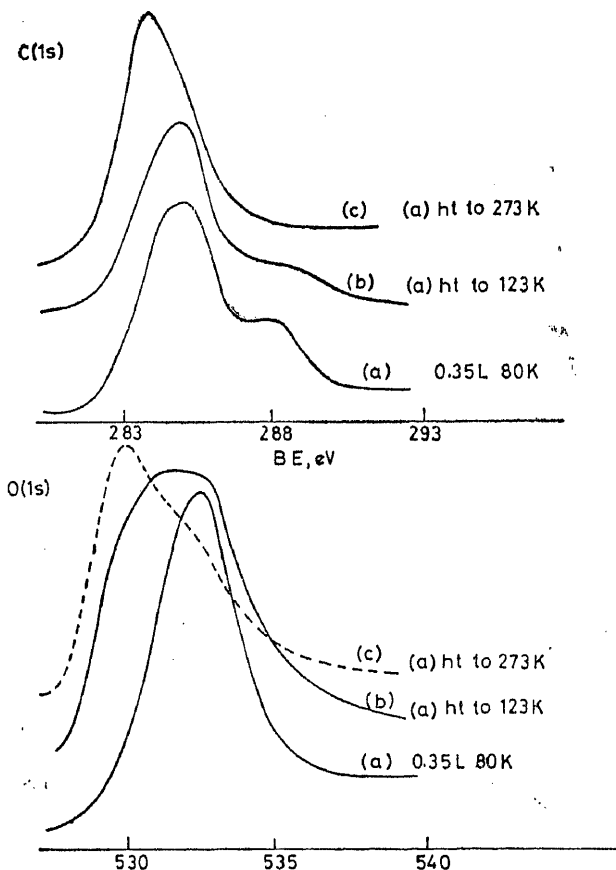


Figure 13. HeII spectra of acetone adsorbed on Cu at different temperatures and exposures. Difference spectra are also shown along with the positions of bands in the gas phase.

appears from the difference spectra at these temperatures (223–323 K), that diethylether undergoes different transformations on these metal surfaces. We are not able to assign the spectra to any definite species at this stage.

3.4. Acetone

HeII spectra of acetone adsorbed on Ni and Cu at 80 K are shown in figures 12 and 13. Difference spectra are also compared with the gas phase spectrum in these figures. It is clear that at 80 K acetone is molecularly adsorbed on both Ni and Cu surfaces. The highest lying lone-pair orbital shows a chemisorption shift towards higher binding energy by about 0.5 eV. Electron states of molecularly adsorbed acetone and their assignments are listed in table 1. The O (1s) bands in xps (figures 14 and 15) appear around 532.5 eV in both the metals; the C (1s) spectrum shows two distinct bands on Ni at 285 and 288 eV corresponding to the two types of carbons (methyl and carbonyl respectively). These bands appear at 291.23 and 293.88 eV in the spectrum of acetone in the gas



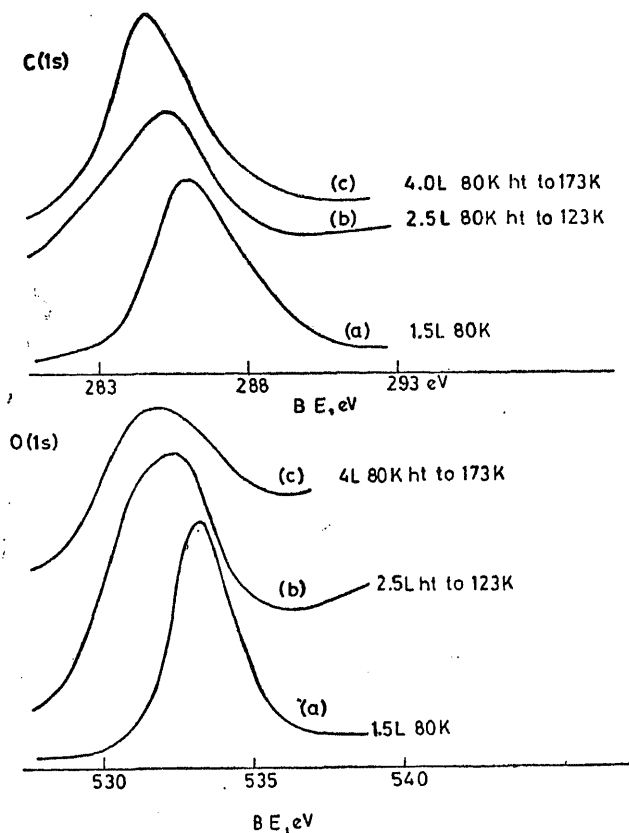


Figure 15. Carbon 1s and oxygen 1s bands in xps of acetone adsorbed on Cu at different temperatures and exposures.

phase (Bakke *et al* 1980). On Cu, the two bands in the **C(1s)** spectrum are not resolved (figure 15).

We notice several changes in UVPS of adsorbed acetone on warming. The resultant changes are noted below :

3.4a : In the case of Cu, on warming to 123 K, uvps shows definitive changes as shown in figure 13. The resulting spectrum is similar to the gas phase spectrum of 2-propanol (figure 13) reported by Katsumata *et al* (1973). The formation of 2-propanol implies surface reduction of acetone. The **C(1s)** and **O(1s)** bands in xps show a shoulder on the lower binding energy side at 123 K.

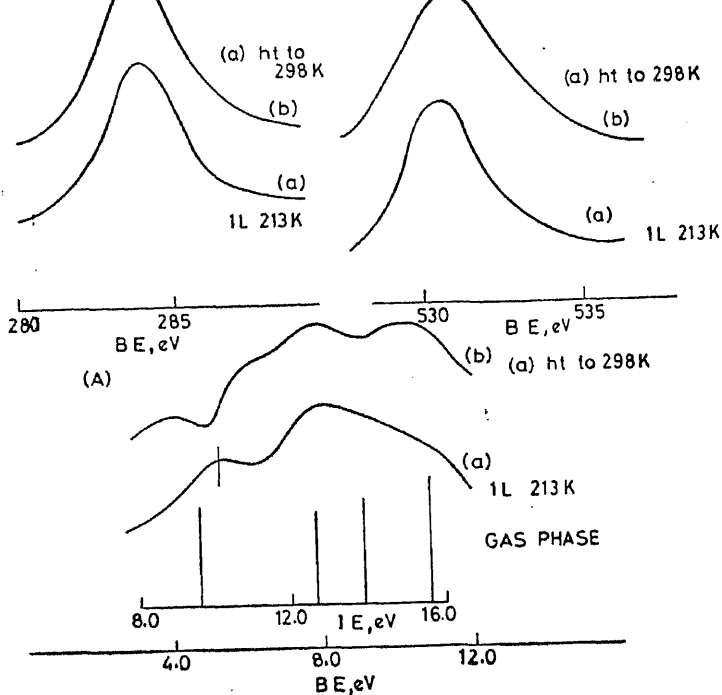


Figure 16. (A) Difference spectra of acetone adsorbed on Fe at different conditions, (B) Carbon 1s bands in xps and (C) Oxygen 1s bands of acetone adsorbed on Fe.

On further warming to 300 K, we notice considerable changes in UVPS; the C(1s) and O(1s) bands are shifted to lower binding energies and suggest the presence of adsorbed CO.

3.4c : Adsorption of acetone on Fe at 213 K shows broad features quite unlike the gas phase acetone spectrum (figure 16). This and the appearance of C(1s) and O(1s) bands in xps at lower binding energies (figure 16) indicate dissociative adsorption of acetone at this temperature. Molecular adsorption occurs only at low temperatures (~ 100 K). Further heating to 300 K results in the appearance of C(1s) and O(1s) at still lower binding energies; these along with the changes observed in UVPS are indicative of the formation of CO species.

3.5. Acetaldehyde

uv photoelectron difference spectra of acetaldehyde adsorbed on Fe are shown in figure 17 along with the gas phase spectrum. Although we could match the observed bands in the difference spectrum against the gas phase spectrum of acetaldehyde, we find that the bands in the difference spectra are much too broad

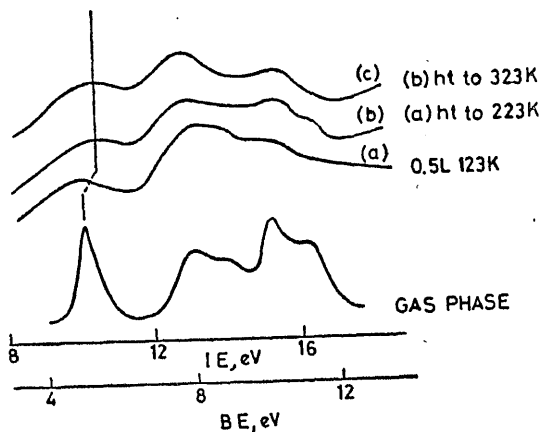


Figure 17. Difference HeII spectra of acetaldehyde adsorbed on Fe at different temperatures and exposures; gas phase spectrum is also shown.

to be due to molecularly chemisorbed species alone. It is possible that there is some decomposition over the entire range 123 K–323 K. However, if we decide to match the 13.2 eV gas phase band with the second band in the difference spectra, we find a lone-pair shift of 0.4 eV due to the molecularly chemisorbed species.

3.6. Methyl acetate

HeII photoelectron spectra of methyl acetate adsorbed on Fe, Ni and Cu at 80 K are shown in figures 18–20. Difference spectra are also compared with the gas phase spectrum (Sweigart and Turner 1972) in these figures. The 12.9 eV band in the gas phase spectrum could be matched with the second band in the difference spectra. The difference spectra show a single band corresponding to the 10.5 eV (n_o) and 11.3 eV (π_{co}) bands in the gas phase. The highest energy band in the region 13.5–14.5 eV that we see in the spectra of the adsorbed species is not found in the gas phase spectrum, since the latter was obtained with HeI excitation. The lone-pair orbital (n_o) shows a chemisorption shift towards higher binding energy of ~ 0.3 eV on all the three metal surfaces. In table 1 we have listed the energies and some of the assignments of UVPS bands of chemisorbed methyl acetate. We see that the lone-pair shift is much lower in methyl acetate than in methanol or acetone.

XPS spectra (figures 21–23) in the C (1s) region show two bands around 285.7 eV and 289.7 eV (290.0 eV for Ni); the band at 285.7 eV is due to methyl carbons while the carbonyl carbon is responsible for the band near 289.0 eV. The band near 285.7 eV is about twice as intense as the 289.7 eV band as expected. This is similar to the two bands observed in the C (1s) and O (1s) regions by Bowker and Madix (1981) and Edwards (1976) in their studies on acetic acid. The O (1s) band appears around 533.1 eV on all the three metals; this is a composite band

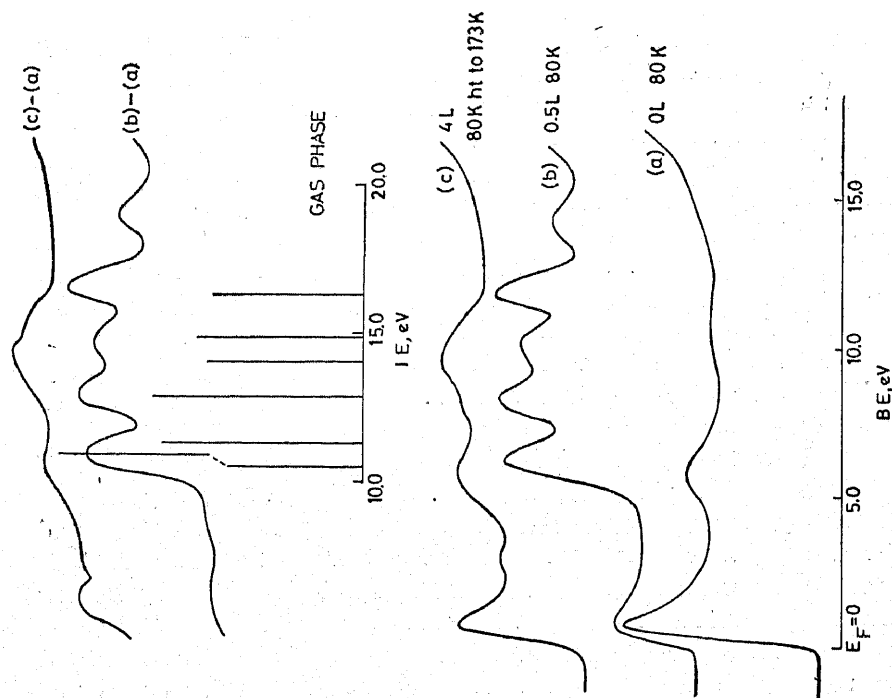


Figure 18. HelI spectra of methyl acetate adsorbed on Fe at different temperatures and exposures. Difference spectra are also shown along with the positions of bands in the gas phase.

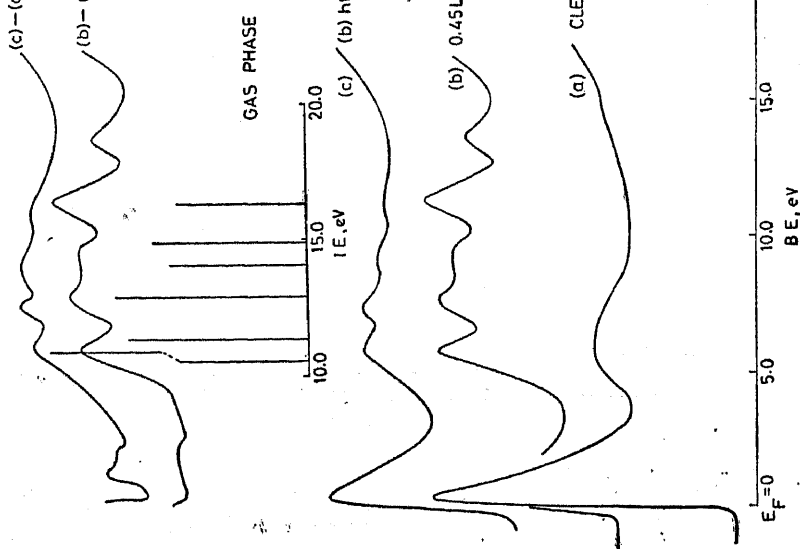
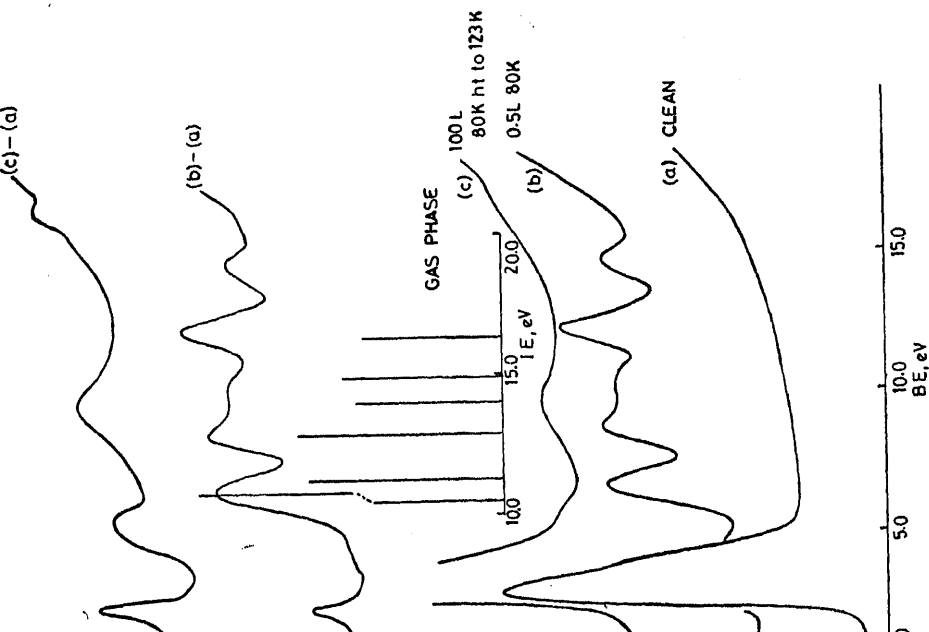


Figure 19. HelI spectra of methyl acetate adsorbed on Ni at different temperatures and exposures. Difference spectra are also shown along with the positions of bands in the gas phase.



HeII spectra of methyl acetate adsorbed on Cu at different exposures and temperatures. Difference spectra are also shown along with ones of bands in the gas phase.

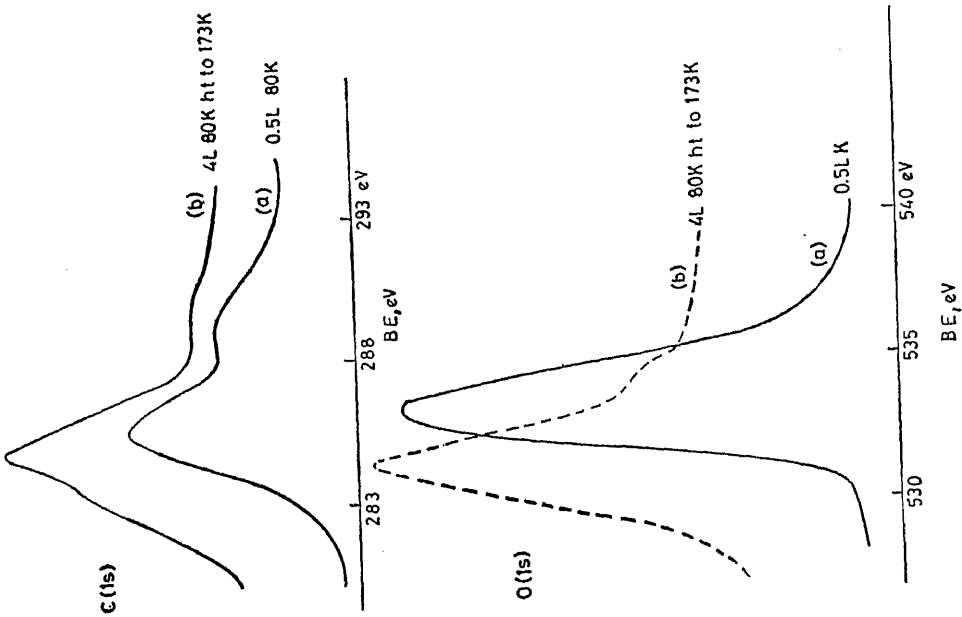


Figure 21. Carbon 1s and oxygen 1s bands in xps of methyl acetate adsorbed on Fe at different temperatures and exposures.

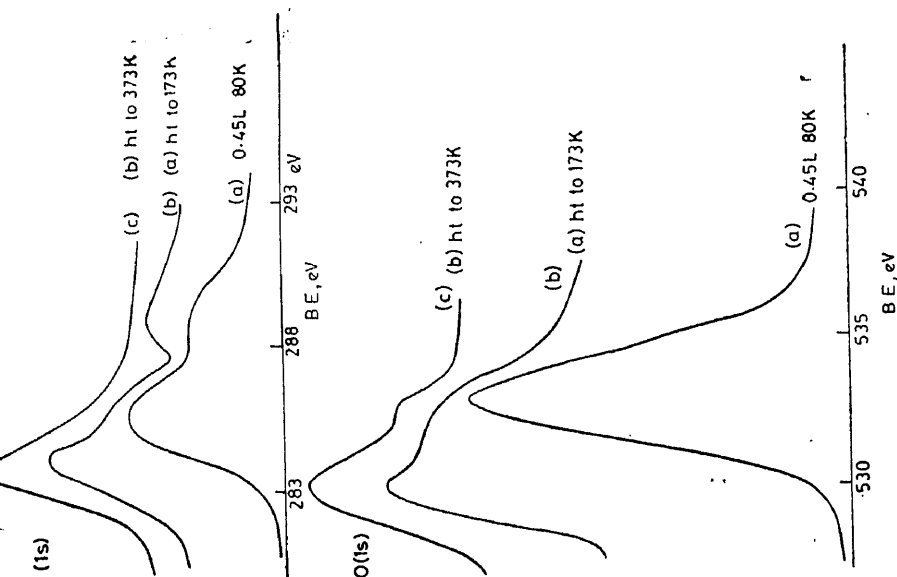


Figure 22. Carbon 1s and oxygen 1s bands in xps of methyl acetate adsorbed on Ni at different temperatures and exposures.

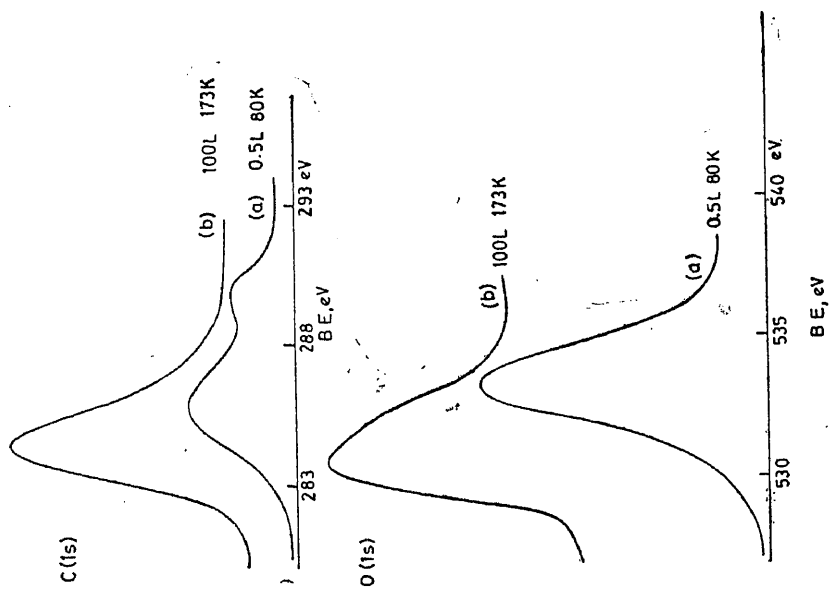


Figure 23. Carbon 1s and oxygen 1s bands in xps of methyl acetate adsorbed on Cu at different temperatures and exposures.

and XPS studies at 80 K clearly establish the presence of molecularly adsorbed methyl acetate on the three metals. We, however, notice significant changes in the spectra on warming the samples.

The main results of thermal effects are as follows :

3.6a : On the Fe surface, heating to 173 K causes drastic changes in the UVPS (figure 18). The resulting spectrum is identical to that of the methoxy species obtained on adsorbing methanol at 223 K. The C (1s) region in XPS shows a band at 284.8 eV while in the O (1s) region we see a band at 531.3 eV. In the case of methanol, we found the C (1s) and O (1s) bands at 284.7 and 531.1 eV respectively. It therefore appears that methyl acetate decomposes to give methoxy species on Fe when warmed to 173 K.

3.6b : On the Ni surface, warming to 173 K results in diffuse bands with features similar to the 80 K spectra in the UVPS (figure 19). In the C (1s) region, we see bands at 285.7 and 289.0 eV and a new band on the low energy side at 284.0 eV. The O (1s) region shows bands at 530.5 and 532.6 eV. These suggest that part of the adsorbed methyl acetate has undergone decomposition.

3.6c : On warming to 123 K, the UVPS of methyl acetate adsorbed on Cu shows drastic changes (figure 20). We see only two bands in the difference spectrum. The difference spectrum is similar to that obtained on warming methanol adsorbed on Cu from 80 K to 123 K wherein we found formation of formaldehyde on the surface. The C (1s) band in XPS appears at 284.6 eV at this temperature and the O (1s) band is broad with the maximum at 530.6 eV and a shoulder at 532.4 eV. At 123 K, methanol adsorbed on Cu shows the C (1s) band at 284.5 eV ; the O (1s) band is broad with a maximum at 532.3 eV and a distinct shoulder at 530.6 eV. The C (1s) and O (1s) bands are as expected of methyl acetate adsorbed at 123 K except that in the latter case the 530.6 eV band is more intense indicating decomposition of methyl acetate. Based on these XPS and UVPS results, we suggest that formaldehyde is formed on warming methyl acetate adsorbed on Cu just as in the case of methanol. It is interesting that adsorption of methyl formate (HCOOCH_3) on Cu at 295 K also yields formaldehyde (Kojima *et al* 1981).

In the adsorption of methyl acetate, only the lone-pair orbital, n_o , shows a relatively small chemisorption shift, but the orbital, π_{co} is unaffected. Methyl acetate, therefore, seems to interact with the metal through the lone-pair orbital of the ether-type oxygen rather than the carbonyl oxygen as shown in chart 2. The sequence of reactions taking place on metal surfaces is also shown in this chart. Formaldehyde could be formed as per sequence (a) on Cu, while methoxy species could be produced as per sequence (b) on Fe. It is interesting that the transformations found in methyl acetate are exactly the same as those found with methanol. In view of this observation (and also because of the small shift of the carbonyl lone-pair orbital energy), we seem to be justified in suggesting bonding through the ether-type oxygen of the ester to the metal in chart 2.

3.7. Ammonia

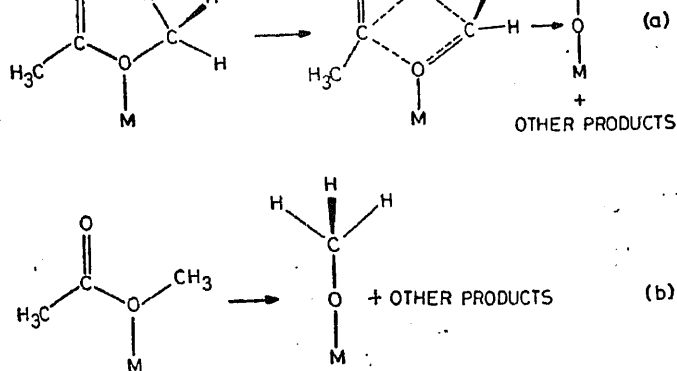


Chart 2. Mechanism of formation of methoxy species and formaldehyde from methyl acetate adsorbed on metals.

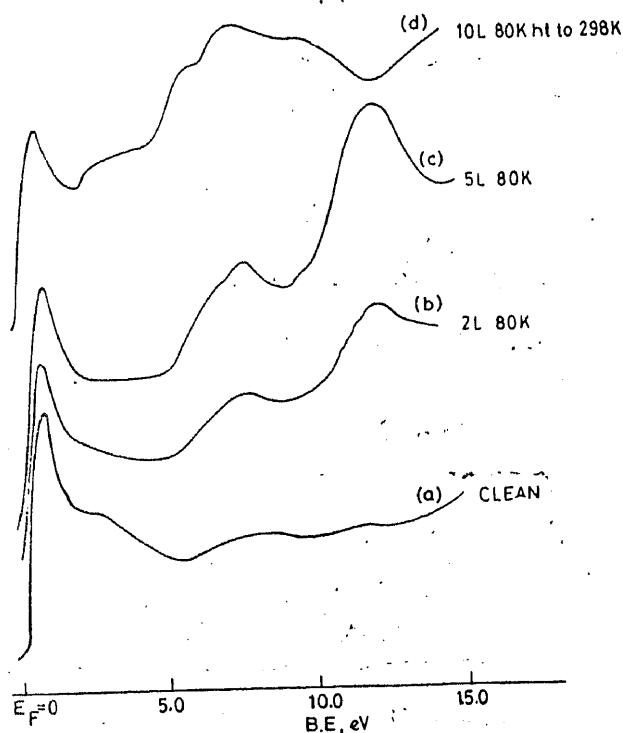
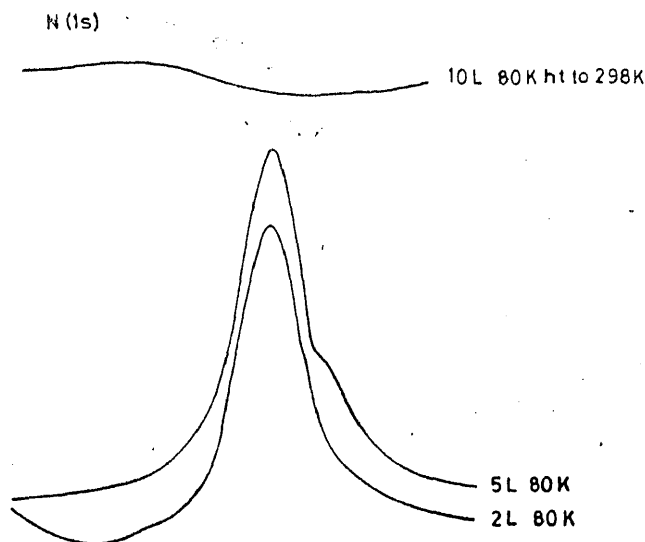


Figure 24. HeII spectra of ammonia adsorbed on Fe at different temperatures and exposures.

pond to the two bands at 10.2 and 14.9 eV in the gas phase spectrum of ammonia. On warming to 298 K, we notice significant changes in the spectrum similar to those reported by Kishi and Roberts (1977) suggesting dissociation of ammonia. The N(1s) signal of molecularly adsorbed species appears around 400 eV (figure 25). On warming this to 298 K, we see a weak band around 397 eV corresponding to a nitrogen species (N or NH) formed due to dissociation of ammonia.

3.8. Methylamine

HeII spectra of methylamine adsorbed on Cu at 80 K and Fe at 173 K are shown in figures 26 and 27. The difference spectra are compared with the HeI gas phase spectrum in these figures. The gas phase spectrum was shifted by ~ 4.4 eV (for Cu) and ~ 4.6 eV (for Fe) so as to obtain the best matching of all the bands between the gas phase and the difference spectra. The highest occupied orbital (lone-pair orbital of nitrogen) on methylamine is shifted towards higher binding energy by 1.0 eV on adsorption on Fe surface and by 0.6 eV on Cu surface. Electron states of adsorbed CH_3NH_2 are tabulated in table 1. XP spectra in the C(1s) region at low temperatures show bands at 286.0 eV (for Cu) and 285.0 eV (for Fe); in the N(1s) region, bands are found at 399.6 eV (for Cu), 399.1 eV (for Fe) as shown in figures 28 and 29. The relatively lower binding energy of the C(1s) peak on Fe could be due to partial decomposition of methylamine at 173 K on this surface. Such decomposition is also indicated by the broad maxima in the UVP difference spectra.



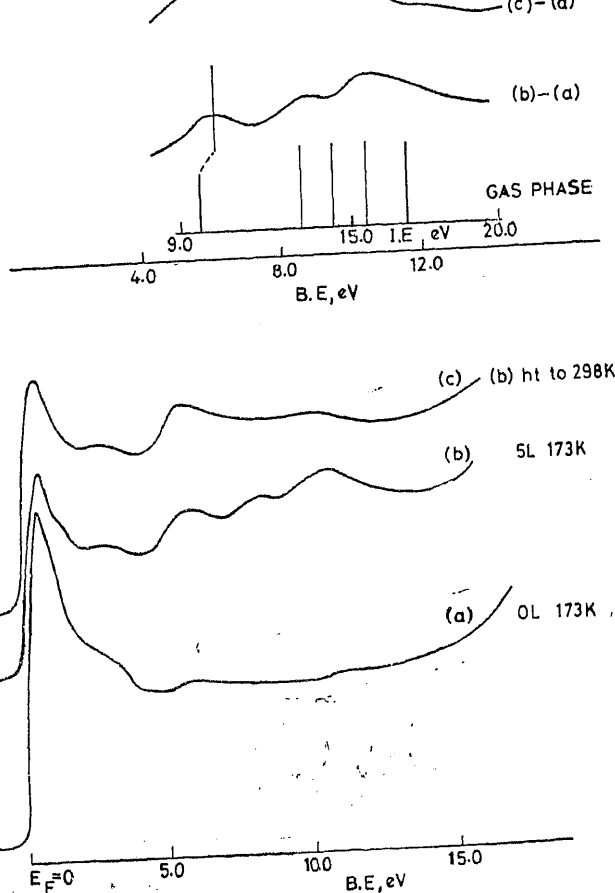


Figure 26. HeII spectra of methylamine adsorbed on Fe at different temperatures and exposures. Difference spectra are also shown along with the positions of bands in the gas phase.

UVPS of $\text{Cu} + \text{CH}_3\text{NH}_2$ show considerable changes on warming to 123 K and C(1s) and N(1s) bands in xps are shifted towards lower binding energies appearing at 285.0 eV and 399.1 eV. These observations suggest occurrence of decomposition of CH_3NH_2 to a nitrogenous species on the metal surface (just as in the case of NH_3). On warming to 300 K, drastic changes are seen in the UVPS on both Cu and Fe surfaces with almost complete disappearance of the bands due to molecular methylamine. The C(1s) band in xps is shifted to 284.0 eV and the N(1s) band shows little or no shift, but the intensity is appreciably lowered.

4. Concluding remarks

(a) All the organic molecules containing lone-pair orbitals that we have examined in the present study adsorb molecularly (associatively) on Fe, Ni and Cu surfaces.

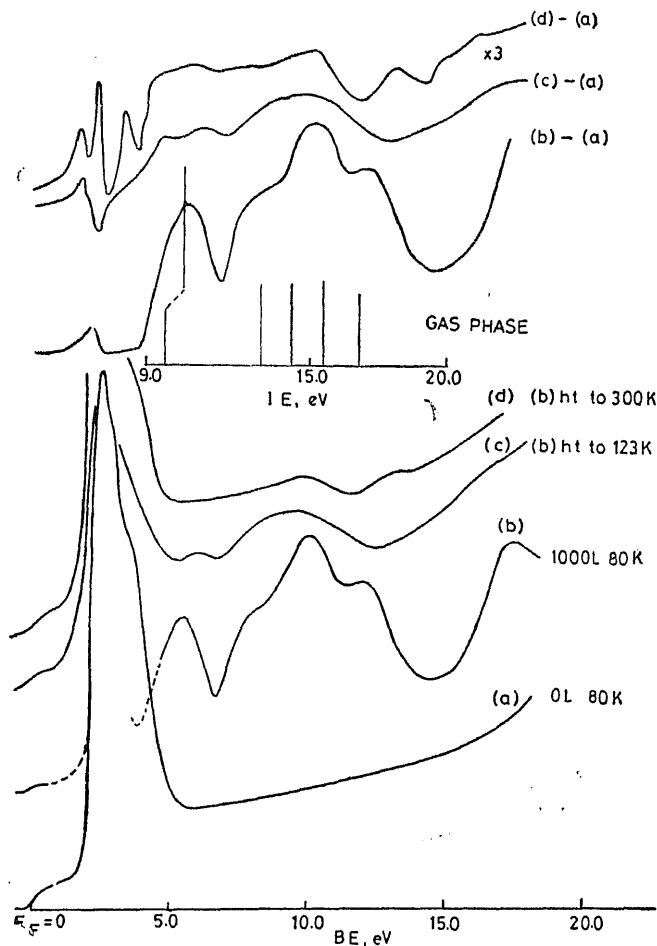


Figure 27. HeII spectra of methylamine adsorbed on Cu at different temperatures and exposures. Difference spectra are also shown along with the positions of bands in the gas phase.

(b) We are able to estimate the stabilization of the lone-pair orbitals due to chemisorption in terms of the increase in its binding energy. These data are presented in table 4 where we have listed the molecules in the order of increasing ionization energy of the lone-pair orbital. The data suggest that the shift generally shows an increasing trend with the decreasing first ionization energy as expected. Furthermore, the stabilization of the lone pair seems to vary as $\text{Fe} > \text{Ni} > \text{Cu}$, decreasing with increasing number of d -electrons, a trend that is not readily understandable.

(c) Chemisorption of molecules gives rise to variation in the core level binding energy of the atom containing the lone pair ($1s$ binding energy of oxygen or

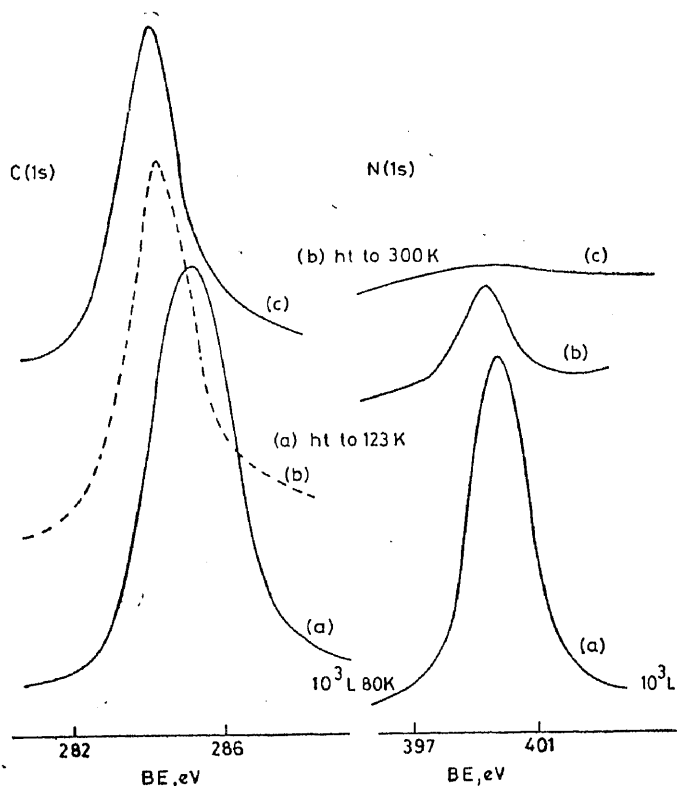


Figure 28. Carbon 1s and nitrogen 1s bands in XPS of methylamine adsorbed on Cu at different temperatures and exposures.

Table 4. Stabilization of the lone-pair orbitals (in eV) on molecular chemisorption.

Molecule	Lone-pair IE	Lone-pair shifts on		
		Fe	Ni	Cu
Methanol	10.8	0.6	0.6	0.5
Methyl acetate	10.5*	0.4	0.3	0.3
Acetone	9.6	..	0.5	0.4
Diethylether	9.6	0.8	..	..
Methylamine	9.6	1.0	..	0.6

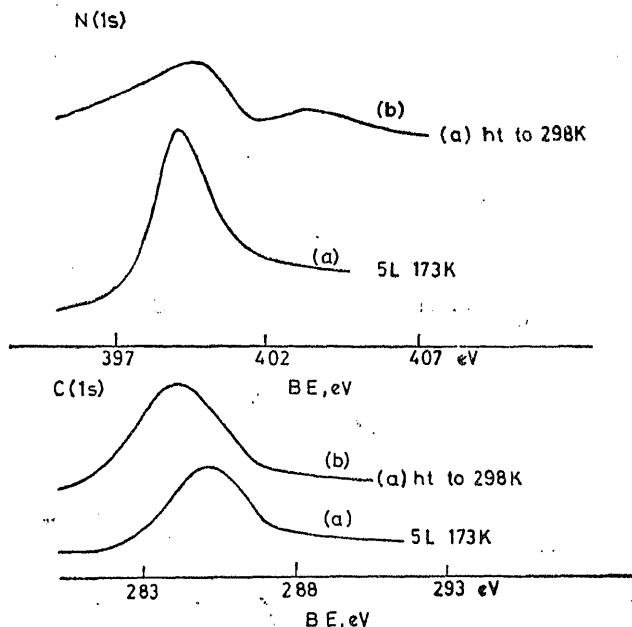


Figure 29. Carbon 1s and nitrogen 1s bands in XPS of methylamine adsorbed on Fe at different temperatures and exposures.

(by matching C(1s) binding energies of adsorbates with those of free molecules), we find the O(1s) binding energy increases by about 0.6 ± 0.2 eV in the case of methanol and acetone adsorbed on the three metal surfaces studied.

(d) Warming the substrate to temperatures above 120 K generally results in the transformation of the adsorbate molecules in all the cases. The nature of the species produced appears to depend on the metal surface and temperature as can be seen from table 2. Methanol gives methoxy species or formaldehyde depending on metal. These transformations are not only reflected in changes in the valence band region (in UVPS) but also in the C(1s) and O(1s) binding energies in XPS. It is interesting that methyl acetate gives the same transformation products on metal surfaces as methanol (table 2). In the case of methylamine we find formation of a nitrogenous species as in ammonia.

(e) The results of our studies on the adsorption of organic molecules find support from Auger studies carried out for the first time in this laboratory (Kamath *et al* 1982b). Thus, Auger spectra also show the transformation of methanol to formaldehyde on Cu surface.

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MNDO study of reaction paths : Hydroboration of carbonyl systems

NABA K RAY* and RITA CHADHA

Department of Chemistry, University of Delhi, Delhi 110 007, India

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Abstract. The hydroboration reactions of acetaldehyde and acetone have been investigated by the MNDO method. The reactions have been shown to be two-step reactions involving an intermediate adduct. This adduct subsequently undergoes hydrogen rearrangement. The hydroboration reactions of acetaldehyde and acetone have been compared with the corresponding reaction of formaldehyde. The charge transfer effects accompanying these reactions have also been discussed.

Keywords. Hydroboration of acetaldehyde and acetone; effect of methyl substitution; charge transfer effects.

1. Introduction

In the year 1939, Brown *et al* demonstrated that diborane reacts rapidly with simple aldehydes and ketones, such as acetaldehyde and acetone, to produce the corresponding dialkoxyboranes (Brown *et al* 1939). Since these substances are readily hydrolysed to form acid and the corresponding alcohol, it is evident that the procedure offers a promising route for the reduction of carbonyl groups. For this reason, we have undertaken a theoretical study on the hydroboration of carbonyl systems.

The results of our study on the hydroboration of formaldehyde (Ray and Chadha 1981) had shown that the reaction is a two-step reaction involving the initial formation of an adduct, followed by its rearrangement to the product *via* a four-centre-like transition state. This latter step was shown to be the rate-determining step. In the present work, we have carried out calculations on the reaction of borane with acetaldehyde and acetone.

2. Method of calculation

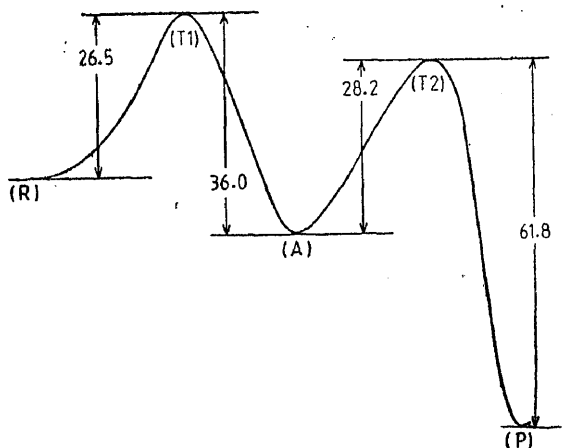
The Modified Neglect of Diatomic Overlap (MNDO) method with the usual parameters (Dewar and Thiel 1977; Dewar and McKee 1977) was employed for

all the calculations reported here. For the methyl group, C_{3v} symmetry was maintained throughout the calculations. All other geometrical parameters were completely optimized. The transition states were located by the energy minimization method (Rothman and Lohr 1980). The incipient C-H bond length was employed as the reaction coordinate and the heat of formation of the systems was plotted as a function of this reaction coordinate. Rothman and Lohr (1980) have shown that the maxima obtained on such reaction surfaces are transition states, provided that the reaction pathway is continuous. The force constant matrix at such points also has only one negative eigenvalue.

3. Results and discussion

The reaction profile for the hydroboration reaction of acetaldehyde with borane (figure 1) indicates two transition states and one intermediate along the reaction pathway. Hence, like the corresponding reaction of formaldehyde, this is a two-step reaction, involving the initial formation of an adduct as a stable intermediate. The activation energy required for its formation is 26.5 kcal/mol, a value much higher than that found (Ray and Chadha 1981) for formaldehyde (9.7 kcal/mol). Thus, the substitution of a hydrogen atom in formaldehyde by a methyl group results in a considerable increase in the activation energy required for the first step. The adduct is more stable than the reactants by 36.0 kcal/mol (c.f. 9.2 kcal/mol for formaldehyde). Methyl substitution, therefore, has only a small effect on the relative stabilities of reactants and adduct. The activation barrier for the second step increases to 28.2 kcal/mol. The reaction enthalpy is -43.1 kcal/mol.

Figure 2 gives the optimized geometries of the four stationary points on the reaction surface. As in the case of formaldehyde, the carbon-oxygen bond distance increases as the reaction proceeds. The B-O bond distance decreases to 1.50 Å in the adduct, after which it increases to a value of 1.53 Å in T2, and



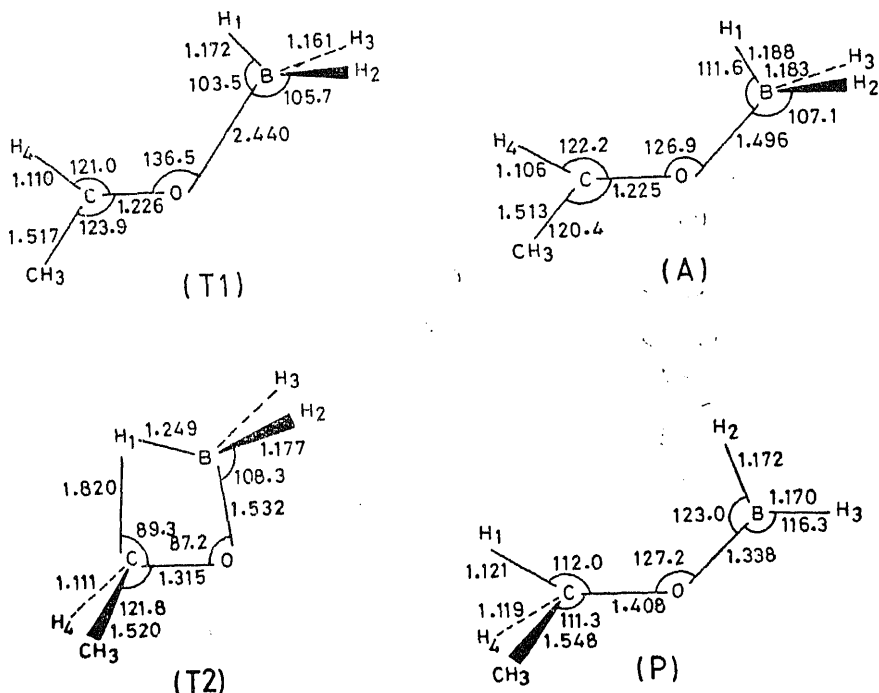


Figure 2. The optimized geometries (in angstroms and degrees) for the transition state (T1) for formation of the adduct, the adduct (A), the transition state (T2) for the formation of product (P) for the hydroboration of acetaldehyde.

then decreases again to a value of 1.34 Å in the product. The COB bond angle decreases from its value of 136.5° in T1 to 87.2° in T2, after which it increases to 127.2° in the product. In this case, too, T2 has a four-centre-like structure.

The hydroboration reaction of acetone, which is the simplest ketone, has also been studied. The profile of this reaction is similar to that of the corresponding reaction of acetaldehyde (figure 3). The first step, the formation of adduct, requires an activation energy of 26.4 kcal/mol. Therefore, the activation barrier for the first step is almost the same for the hydroboration of acetaldehyde and acetone. The second step proceeds with an activation energy of 31.3 kcal/mol. The reaction enthalpy is -36.2 kcal/mol.

Figure 4 gives the optimized geometry of each stationary point on the reaction surface. As expected, the carbon-oxygen bond distance increases as the reaction proceeds. The B-O bond distance is 1.49 Å in the adduct, after which it increases to a value of 1.52 Å in T2, and then decreases to 1.34 Å in the product. The COB bond angle also decreases from its value of 144.7° in T1 to 89.2° in T2, after which it increases to 126.9° in the product. T2 again has a four-centre-like structure. Comparison of figure 2 with figure 4 indicates that the geometries at the stationary points are essentially similar for both the reactions studied here.

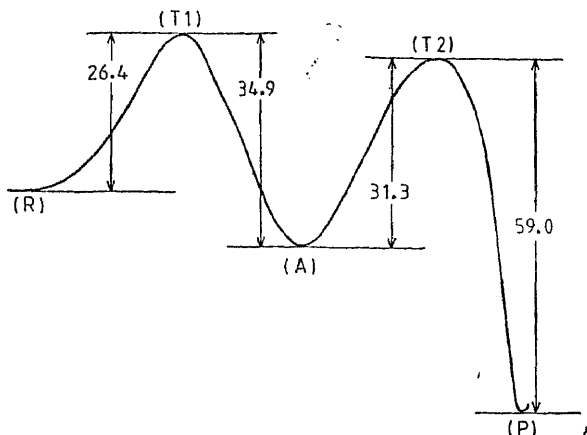


Figure 3. The energy profile (kcal/mol) for the reaction of acetone with borane.

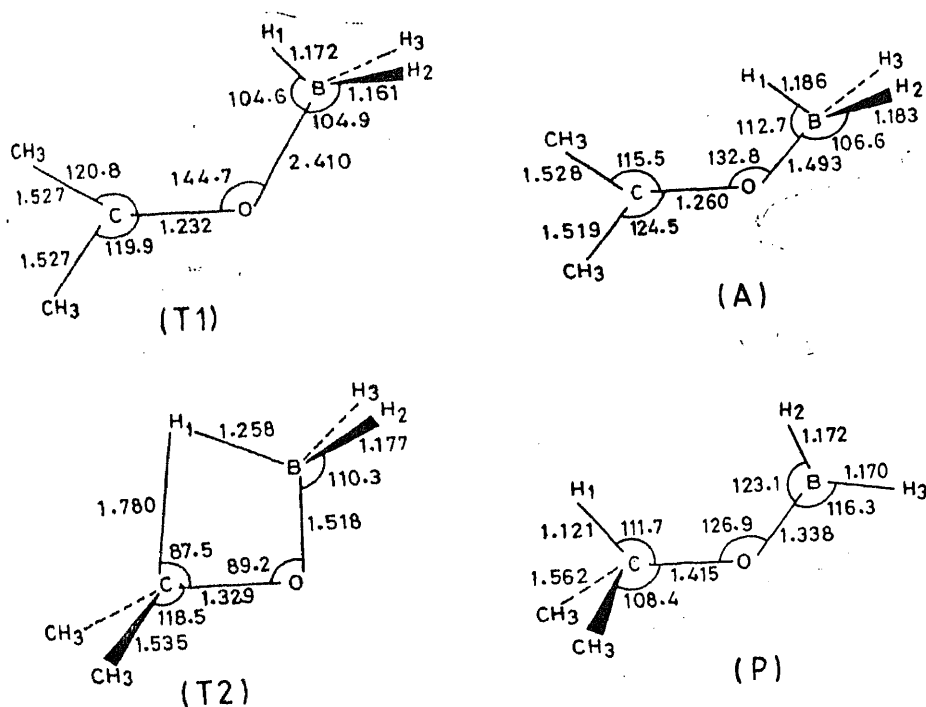


Figure 4. The optimized geometries (in angstroms and degrees) for the stationary points on the reaction surface for hydroboration of acetone.

4. Charge transfer effects

The charges on various atoms in the stationary points on the potential surface for

Atom ^b	Charge				
	<i>R</i>	<i>T1</i>	<i>A</i>	<i>T2</i>	<i>P</i>
C	0·24	0·27	0·29	0·41	0·17
O	-0·28	-0·31	-0·03	-0·24	-0·25
B	0·24	0·23	-0·21	-0·15	0·11
H ₁	-0·08	-0·13	-0·12	-0·11	0·00
H ₂	-0·08	-0·09	-0·06	-0·03	-0·05
H ₃	-0·08	-0·04	-0·07	-0·03	-0·02
H ₄	0·01	0·03	0·09	0·06	0·02
CH ₃	0·03	0·04	0·11	0·09	0·02

^a see figure 1

^b see figure 2.

Table 2. Charges on various atoms in the stationary points on the reaction surface^a for hydroboration of acetone.

Atom ^b	Charge				
	<i>R</i>	<i>T1</i>	<i>A</i>	<i>T2</i>	<i>P</i>
C	0·19	0·23	0·25	0·39	0·13
O	-0·29	-0·31	-0·04	-0·26	-0·24
B	0·24	0·23	-0·20	-0·13	0·10
H ₁	-0·08	-0·13	-0·12	-0·14	0·02
H ₂	-0·08	-0·09	-0·07	-0·03	-0·05
H ₃	-0·08	-0·05	-0·07	-0·03	-0·02
(CH ₃) ₁	0·05	0·06	0·11	0·10	0·03
(CH ₃) ₂	0·05	0·06	0·14	0·10	0·03

^a see figure 3

^b see figure 4

Table 3. Heats of formation at stationary points on the reaction surface^a for hydroboration of carbonyl systems.

Point	Heat of formation (kcal/mol)	
	Acetaldehyde	Acetone
<i>R</i>	-30.6	-37.1
<i>T1</i>	-4.1	-10.7
<i>A</i>	-40.1	-45.6
<i>T2</i>	-11.9	-14.3
<i>P</i>	-73.7	-73.3
<i>EA</i> ^b (kcal/mol)	28.2	31.3

^a see figures 1 and 3.

^b Energy of activation for the rate-determining step.

The progress of the reaction from *T1* to *A* is accompanied with an increase in charge density on the boron atom by 0.44 units. The total amount of charge transferred from acetaldehyde to borane, in the adduct, is 0.46 units. In *T2*, the amount of charge transferred reduces to 0.32 units, due to back donation of charge to the oxygen atom.

The charges on various atoms in the stationary points on the potential surface for hydroboration of acetone are listed in table 2. In this case, the amounts of charge transferred from acetone to borane in *T1*, *A* and *T2* are, respectively, 0.04, 0.46 and 0.33 units.

In all the cases, therefore, the adduct is a charge transfer complex and the amount of charge transfer from the carbonyl system to borane is nearly constant.

5. Conclusions

The present study has indicated that the reaction path for the hydroboration of aldehydes and ketones includes an intermediate charge transfer adduct and two transition states. The pronounced effect of substitution of one hydrogen atom of formaldehyde by a methyl group on the activation barrier to the first step is probably due to steric factors. Unlike the case of nitriles (Chadha and Ray 1982) the transition state for the first step is more susceptible to steric hindrance.

The results of the present work are in agreement with the mechanism proposed by Brown and Subba Rao (1960). As expected, methyl substitution increases the stability of the adduct (table 3). The electron donating property of the methyl group is responsible for this effect. Like the hydroboration reaction of formal-

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Infrared and Raman spectra and thermodynamic functions of 4-methoxypyridine N-oxide*

K C MEDHI

Department of Physics, Gauhati University, Gauhati 781 014, India

MS received 24 February 1982

Abstract. The infrared spectrum of 4-methoxypyridine N-oxide in the region 4000–30 cm^{-1} in the solid and liquid states and the polarized laser Raman spectrum of the molecule in the liquid state have been investigated. A vibrational assignment of the observed frequencies based on the state of polarization of the Raman lines and comparison with the related molecules is presented. Ideal gas state thermodynamic functions of the molecule are calculated in the temperature range 273–1500° K.

Keywords. Infrared spectrum ; Raman spectrum ; thermodynamic functions ; 4-methoxypyridine N-oxide.

1. Introduction

As a part of the earlier investigations on the vibrational assignments for some substituted pyridine molecules (Medhi *et al* 1965 ; Medhi 1965, 1972, 1977), the infrared and Raman spectra of 4-methoxy pyridine N-oxide have been studied in the present work. The infrared spectrum of this molecule in a limited frequency range was reported by Hideyo Shindo (1958), Costa and Blasina (1955) and Ghersetti *et al* (1973), and only a few frequencies were assigned. There is, however, no earlier study on the Raman spectrum of 4-methoxypyridine N-oxide.

The present paper gives a detailed account of the infrared and Raman spectra of the molecule of 4-methoxypyridine N-oxide, and a vibrational assignment of the observed frequencies, based on the polarization of the Raman lines and comparison with the assignments proposed for other related molecules (Green 1962 ; Green *et al* 1963 ; Long and George 1963 ; Allan *et al* 1971 ; Berezin and Elkin 1973 a) is presented. The ideal gas state thermodynamic properties of the molecule are also calculated on the basis of this vibrational assignment.

2. Experimental

The sample of 4-methoxypyridine N-oxide was supplied by Aldrich Chemical Company, U.S.A. It was purified by repeated sublimation in vacuum.

equipped with an argon ion laser. The 514.5 nm (200 mw) was used to excite the spectrum. The polarization of the Raman lines was measured by the same method as described previously (Medhi 1977). A Carl-Zeiss Specord IR 75 spectrophotometer was employed to measure the mid infrared spectrum in the range 4000-400 cm^{-1} either in hexachlorobutadiene (HCB) or in nujol mull as well as in thin liquid film prepared from the melt of the substance. The far infrared spectrum from 500 to 30 cm^{-1} was obtained in nujol mull using a Perkin-Elmer Model 180 spectrophotometer. Because of the high boiling point of the substance, the vapour-phase infrared spectrum could not be obtained.

3. Results and discussion

Table 1 gives the details of the infrared and Raman spectra of 4-methoxypyridine N-oxide together with the probable assignments for the observed frequencies. The fundamental frequencies are summarized in table 2. The calculated values of the thermodynamic functions are listed in table 3.

Table 1. Observed infrared and Raman frequencies and assignments for 4-methoxypyridine N-oxide.

Infrared (cm ⁻¹)		Raman (cm ⁻¹)		Assignment
HCB or nujol mull	Melt	Melt		
3112 (s)	3108 (s)	3092 (3) p	$\nu_1 (a')$	
3065 (mw)	3060 (mw)		$\nu_2 (a')$	
3041 (s)			$\nu_3 (a')$	
3026 (ms)	3025 (s)	3022 (1) p	$\nu_4 (a')$	
2997 (mw)			$\nu_{20} (a'')$, -CH ₃ asymmetric stretching	
2951 (mw)	2943 (mw)	2948 (1) p	$\nu_5 (a')$, -CH ₃ asymmetric stretching	
2932 (w)			$2 \times \nu_{11} (A')$	
2897 (mw)	2895 (mw)	2901 (0)	$\nu_{11} + \nu_{12} (A')$	
2847 (ms)	2840 (s)	2845 (2) p	$\nu_6 (a')$, -CH ₃ symmetric stretching	
2812 (w)			$\nu_9 + \nu_{13} (A')$	
2785 (ms)	2769 (ms)		$\nu_{11} + \nu_{13} (A')$	
2581 (w)	2571 (w)		$\nu_8 + \nu_{20} (A')$	
	2509 (w)		$\nu_9 + \nu_{20} (A')$	
2235 b (ms)			$\nu_{10} + \nu_{19} (A')$	
2045 (mw)	2038 (ms)		$\nu_{14} + \nu_{24} (A')$	
2011 (w)			$\nu_{17} + \nu_{23} (A')$	
1941 (w)	1927 (w)		$\nu_{17} + \nu_{24} (A')$	
1903 (mw)			$\nu_{12} + \nu_{20} (A')$	
1889 (sh)			$\nu_{19} + \nu_{23} (A')$	
	1877 (mw)		$\nu_{20} + \nu_{22} (A')$	
	1755 (w)		$\nu_{18} + \nu_{25} (A')$	
			$\nu_{33} + \nu_{34} (A')$	

Table 1 (Contd.)

Infrared (cm ⁻¹)		Raman (cm ⁻¹)		Assignment	
HCB or nujol mull	Melt	Melt			
1623 (s)	1625 (s)	1624 (3) p	ν_7 (a')		
1566 (sh)	1569 (sh)		$\nu_{18} + \nu_{26}$ (A')		
1563 (ms)	1557 (ms)	1559 (1) p	ν_8 (a')		
1520 (sh)	1520 (sh)		$\nu_{22} + \nu_{25}$ (A')		
1509 (sh)	1510 (sh)		$2 \times \nu_{24}$ (A')		
1496 (vs)	1490 (vs)	1490 (0) p	ν_9 (a')		
1471* (s)	1466† (ms)		ν_{10} (a') and ν_{30} (a''), — CH ₃ asymmetric deformations		
1462* (vs)	1455† (ms)	1458 (0) p = 0.73	ν_{11} (a'), — CH ₃ symmetric deformation		
1439 (s)	1441 (s)	1442 (sh)	ν_{12} (a')		
		1415 (0) p	$\nu_{17} + \nu_{28}$ (A')		
1319 (ms)	1310 (sh)	1310 (sh) p = 0.63	ν_{13} (a')		
1298 (vs)	1289 (vs)	1290 (2) p	ν_{14} (a')		
1291 (vs)			ν_{15} (a')		
1233 (ms)			ν_{16} (a'), — N—O stretching		
1205 (vs)	1227 (vs)		$\nu_{35} + \nu_{40}$ (A')		
1188 (sh)		1184 (sh) p	ν_{17} (a')		
1180 (s)	1172 (s)	1175 (4) p	$\nu_{25} + \nu_{26}$ (A')		
	1124 (w)		ν_{18} (a')		
1111 (w)	1099 (s)	1102 (0) p	ν_{31} (a''), — CH ₃ out-of-plane rocking		
1033 (s)		1058 (0) dp	ν_{19} (a')		
1014 (vs)	1022 (vs)	1027 (1) p	ν_{20} (a') and ν_{21} (a'), — O—CH ₃ stretching		
962 (w)	955 (w)		ν_{32} (a')		
900 (w)	897 (w)		ν_{33} (a')		
856 (sh)	855 (sh)	858 (10) p	ν_{22} (a'), — N—O in-plane deformation		
850 (vs)			ν_{34} (a')		
836 (sh)	840 (vs)	842 (sh) p	ν_{23} (a'), — CH ₃ in-plane rocking		
811* (ms)	~ 810 (sh)		ν_{35} (a'')		
756 (vs)	758 (vs)	758 (0) p	ν_{24} (a')		
690 (mw)	704 (w)	708 (0) dp	ν_{36} (a'')		
657 (mw)	657 (mw)	661 (1) p = 0.74	ν_{25} (a')		
586 b (s)			?		
542 (w)	540† (w)	541 (0) dp	ν_{37} (a''), — N—O out-of-plane deformation		
522 (s)	526 (ms)	530 (0) dp	ν_{38} (a'')		
462 (ms)	463 (ms)	465 (0) p	ν_{26} (a'), $\angle$ COC deformation		
420 (sh)			ν_{39} (a'')		
405 (ms)		406 (1) p	ν_{27} (a')		
376 (mw)		370 (0) dp	ν_{40} (a''), $\angle$ COC deformation		
252 (mw)		244 (0) p	ν_{28} (a')		
198 b (ms)			ν_{42} (a'')		
148 (mw)			{ lattice modes		
85 (mw)					
47 (w)					

* Frequency observed in solid film prepared from the melt.

Symmetry species	Mode No. (Wilson 1934)	Fund.	Wavenumber (cm ⁻¹)
<i>a'</i>	20b	ν_1	3092
	2	ν_2	3060
	20a	ν_3	3041
	7b	ν_4	3022
		ν_5	2948
		ν_6	2845
	8a	ν_7	1624
	8b	ν_8	1559
	19a	ν_9	1490
		ν_{10}	1466
		ν_{11}	1458
	19b	ν_{12}	1441
	14	ν_{13}	1310
	13	ν_{14}	1290
	3	ν_{15}	1233
		ν_{16}	1227
	9a	ν_{17}	1175
	15	ν_{18}	1102
	18a	ν_{19}	1033
	1	ν_{20}	1027
		ν_{21}	(1027)
		ν_{22}	858
		ν_{23}	840
	12	ν_{24}	758
	6b	ν_{25}	661
		ν_{26}	465
	6a	ν_{27}	406
	18b	ν_{28}	244
<i>a''</i>		ν_{29}	2997
		ν_{30}	(1466)
		ν_{31}	1058
	17a	ν_{32}	955
	5	ν_{33}	897
	10a	ν_{34}	850
	10b	ν_{35}	811
	4	ν_{36}	708
		ν_{37}	541
	11	ν_{38}	530
	16a	ν_{39}	420
		ν_{40}	370
		ν_{41}	?
	16b	ν_{42}	198

() Frequency assigned more than once.

? Frequency not assigned.

Temperature (° K)	C_p Cal/degree/ mole	T Cal/degree/ mole	T Cal/degree/ mole	T Cal/degree/ mole
273.15	26.93	15.45	81.58	66.13
298.15	29.43	16.52	84.04	67.53
300	29.61	16.60	84.22	67.63
400	39.06	21.06	94.06	73.01
500	47.03	25.48	103.67	78.19
600	53.46	29.63	112.83	83.20
700	58.65	33.42	121.47	88.06
800	62.89	36.84	129.59	92.75
900	66.40	39.94	137.20	97.27
1000	69.35	42.74	144.36	101.62
1100	71.83	45.27	151.09	105.82
1200	73.93	47.58	157.43	109.86
1300	75.73	49.67	163.42	113.75
1400	77.27	51.59	169.09	117.50
1500	78.60	53.35	174.47	121.12

* Ideal gas state at standard pressure of 1 atm.

The molecule of 4-methoxypyridine N-oxide is assumed to have the C_s symmetry with $28a'$ and $14a''$ normal modes of vibrations predicted from group theoretical considerations. All the forty-two normal vibrations are active both in the infrared and Raman spectra. The Raman lines of a' species should be polarized, and those belonging to the a'' species depolarized.

3.1. Pyridyl vibrations

3.1a *Class a'* : There appear four frequencies in the C-H stretching region. These are readily assigned to such valence oscillations. The polarized Raman lines observed at 1624 , 1559 and 1490 cm^{-1} and the strong infrared band at 1439 cm^{-1} may be attributed to the modes primarily derived from the stretching of the ring. The infrared spectrum shows very strong absorption at 1291 cm^{-1} ; its Raman counterpart located at 1290 cm^{-1} is polarized. This may be confidently assigned to the mode characterised as C-O stretching in agreement with the assignments made in the case of other molecules (Katritzky and Coats 1959; Briggs *et al* 1957; Sax *et al* 1960; Spinner and White 1962; Katritzky 1959). Two other substituent-sensitive modes belonging to the a' class may be identified with the polarized Raman lines at 758 and 244 cm^{-1} . Infrared bands of medium strength are observed at 657 and 405 cm^{-1} . The corresponding Raman line at 661 cm^{-1} appears to be depolarized and that at 406 cm^{-1} is polarized. These may be reasonably assigned to the planar ring angle deformation modes (Green *et al* 1963; Berezin and Elkin 1973a). The remaining modes belonging to the a' class may be

and the moderately intense infrared band at 1233 cm^{-1} .

3.1b Class a'' : The Raman lines observed at 708 and 530 cm^{-1} are depolarized and are assigned as a'' fundamentals arising principally from the out-of-plane bending motions of the ring carbon atoms and the ring hydrogen atoms respectively. The remaining a'' modes are identified with the observed infrared frequencies at 962 , 900 , 850 , 811 , 420 and 198 cm^{-1} in agreement with the assignments proposed for related molecules (Medhi 1977 ; Green *et al* 1963 ; Long and George 1963).

3.2. N-O vibrations

The infrared spectrum shows very strong absorption at 1205 cm^{-1} , this may be attributed to the mode that involves the stretching of the N-O bond in agreement with the previous assignment (Costa and Blasina 1955). The in-plane N-O deformation mode is unambiguously assigned to the intensely strong polarized Raman line at 858 cm^{-1} , whilst the out-of-plane bending mode may be responsible for the depolarized Raman shift observed at 541 cm^{-1} (Berezin and Elkin 1973 b ; Katritzky and Coats 1959 ; Wiley and Slaymaker 1957 ; Colthup *et al* 1975).

3.3. OCH_3 vibrations

The two components of the out-of-phase CH_3 stretching mode may be assigned to the polarized Raman shift observed at 2948 cm^{-1} and the moderately intense infrared band at 2997 cm^{-1} , while the symmetric stretching mode is identified with the polarized Raman line at 2845 cm^{-1} (Green 1962 ; Badger and Moritz 1959 ; Pozefsky and Coggeshall 1951 ; Wiberley *et al* 1960 ; Henbest *et al* 1957 ; Seth-Paul *et al* 1974). It is known that the symmetric CH_3 deformation mode, being somewhat sensitive to the electronegativity of the attached oxygen atom in the O-CH_3 group, shifts to higher frequency (Sheppard 1955 ; Bellamy and Williams 1956 ; Wilmschurst 1957). Thus the infrared band appearing with considerable intensity at 1462 cm^{-1} is reasonably assigned to this mode. The CH_3 asymmetric deformations may be responsible for the observed frequency at 1471 cm^{-1} . While the assignments of the CH_3 rocking modes are less certain, the torsional mode is not located in this case.

In methoxy compounds usually a strong band appears in the interval 1050 – 1010 cm^{-1} which has been interpreted as O-CH_3 stretching fundamental (Katritzky and Coats 1959 ; Briggs *et al* 1957 ; Sax *et al* 1960 ; Spinner and White 1962). In agreement with this the strong infrared band observed at 1014 cm^{-1} is assigned to such mode. The in-plane and out-of-plane O-CH_3 deformation may be represented by the polarized Raman line at 465 cm^{-1} (Allan *et al* 1971) and the depolarized Raman shift observed at 370 cm^{-1} , respectively.

In addition to these, the infrared spectrum shows strong but somewhat broad absorption at 586 cm^{-1} in the solid state ; but the band completely disappears on melting the substance by raising the temperature, or when the compound is dissolved in methylene chloride. Therefore, it cannot be assigned as a fundamental or a combination band. This may, however, arise from some overtone band.

Besides the above fundamental frequencies, the infrared and Raman spectra of 4-methoxypyridine N-oxide show some weaker bands which are interpreted as overtones and combination bands.

4. Thermodynamic properties

Ideal gas state thermodynamic functions of 4-methoxypyridine N-oxide were determined at several temperatures between 273.15 and 1500° K using the fundamental frequencies given in table 2 and the following structural parameters and relative atomic masses :

C-C = 1.397 Å, C-H = 1.084 Å, N-O = 1.37 Å, $\angle$ CCC = $\angle$ CNC = $\angle$ CCH = $\angle$ CNO = $\angle$ COC = 120°.

For OCH₃ group -C-H = 1.0936 Å, C-O = 1.426 Å, and all angles are tetrahedral.

H = 1.0079, C = 12.011, O = 16.0, N = 14.01 amu.

The rotational constants and the reduced moment of inertia of the methyl group, as calculated from the structure defined above, were found to be $A = 0.14860 \text{ cm}^{-1}$, $B = 0.03347 \text{ cm}^{-1}$, $C = 0.02746 \text{ cm}^{-1}$ and $I_m = 5.2668 \times 10^{-40} \text{ gm cm}^2$. The thermodynamic functions were calculated by assuming a rigid rotor, harmonic oscillator approximation and free internal rotation of the methyl group.

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Carbon-13 nuclear magnetic resonance studies on high spin iron(III) porphyrins

D V BEHERE and S MITRA*

Chemical Physics Group, Tata Institute of Fundamental Research, Colaba,
Bombay 400 005, India

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Abstract. Carbon-13 NMR studies on a series of high spin iron(III) porphyrins, namely tetraphenylporphyrin iron(III) halides [Fe(TPP) X, X = Cl, Br, I] in CDCl₃ solution are reported. As expected the ¹³C shifts are found to be an order of magnitude larger than the corresponding proton shifts. The dipolar contribution, which is quite important for the proton NMR, becomes much less significant for the ¹³C shifts. No systematic variation in the ¹³C shift across the series is observed, except for the meso-carbon which shows a small but gradual decrease in going from the chloro to the iodo complex. The ¹³C shift for the various carbon atoms of the porphyrin ligand shows interesting pattern which is discussed in terms of spin delocalisation mechanisms.

Keywords. Nuclear magnetic resonance ; high spin iron(III) porphyrins ; C-13 shifts.

1. Introduction

Nuclear magnetic resonance (NMR) studies on synthetic iron porphyrins have been very useful in understanding the magnetic and electronic properties of iron in haem proteins (Wuthrich and Baumann 1973a,b, 1974 ; Goff 1978, 1981 ; LaMar and Walker 1979). Most of the NMR studies on iron porphyrins have been done on proton nucleus. ¹³C NMR is, however, a more direct, sensitive and accurate probe for paramagnetic complexes. Besides being a direct probe to the distribution of unpaired spin across the porphyrin skeleton, ¹³C NMR has an additional advantage over proton NMR. Since the ¹³C shifts are generally an order of magnitude larger than the corresponding proton shifts (Horrocks 1973 ; Doddrell and Gregson 1974 ; Mitra 1977) the dipolar contribution to the ¹³C shifts is expected to be usually negligible, which makes the interpretation of the data easier.

We have recently reported (Behere *et al* 1982) a detailed proton NMR study on a series of five coordinated high spin tetraphenylporphyrinato iron(III) halides, [Fe(TPP)X, X = Cl, Br, I (figure 1)]. These studies confirmed the dominant

* To whom correspondence should be made.

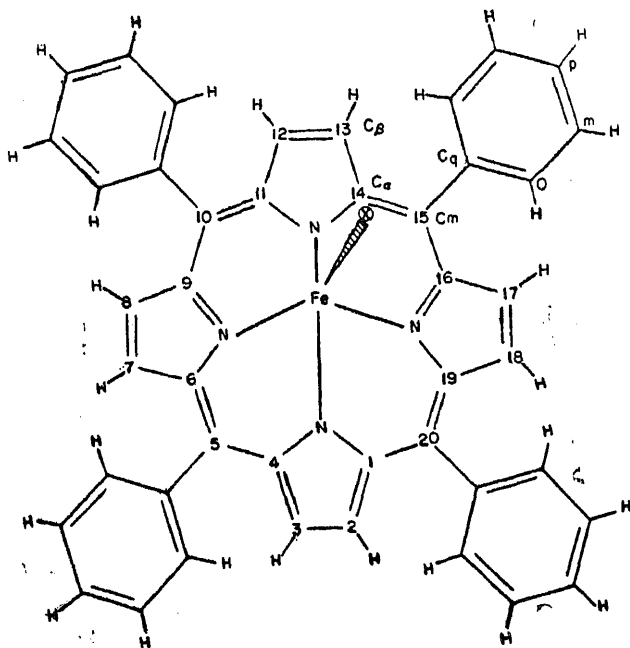


Figure 1. Molecular geometry of Fe(TPP)X.

influence of the porphyrin ligand on the shift pattern, since the changes in the axial halide ligand were found to have minimal effect on the shifts of the various protons. Based on the pattern of the unpaired spin density distribution across various proton sites, a mechanism for the delocalisation of the unpaired spin across the porphyrin ligand was suggested (Behere *et al* 1982). The present ^{13}C NMR study is an extension of our proton NMR study (Behere *et al* 1982) and forms a part of our research programme on metalloporphyrins (Behere and Mitra 1979, 1980; Behere *et al* 1977, 1979, 1981, 1982). ^{13}C NMR on Fe(TPP)Cl had been reported earlier by Goff (1978) but a subsequent study by Mispelter *et al* (1979) proved that the previous assignments were grossly in error.

2. Experimental

The Fe(TPP)X samples were prepared by the previously reported methods (Adler *et al* 1970). ^{13}C NMR in natural abundance was recorded at 67.89 MHz on Bruker FT NMR spectrometer. Deuterated chloroform solutions having solute concentrations in 30–60 mM were used. Since aggregation effect often complicates the ^{13}C NMR results on metalloporphyrins, a study at different concentrations was done to determine the optimum concentration range. Spectral width of about 50,000 Hz were employed. About 30,000–40,000 transients were collected. Pulses of 15 μsec width were applied at a rate of 0.4 sec repetition. The spectra were run under conditions of proton broad band decoupling with use of 8/8 K memory

believed to be shifted to 1000–1400 ppm down-field and hence could not be observed simultaneously along with other resonances. As in the proton NMR study the two ortho and meta carbons of the phenyl ring show inequivalence with respect to the iron atom which lies out of the mean porphyrin plane. Table 1 summarises the relevant ^{13}C shifts on the three complexes; the data were corrected for diamagnetic shifts using the corresponding values of ZnTPP (Wuthrich and Baumann 1973a). The proton NMR shifts are included in table 1 for comparison.

The ^{13}C shifts consist of both dipolar and contact terms. The dipolar contribution is given in axial symmetry by

$$\left(\frac{\Delta H}{H}\right)_D = \frac{1}{3N} (K_{\perp} - K_{\parallel}) \left[\frac{3\cos^2\theta - 1}{r^3} \right], \quad (1)$$

where $(K_{\perp} - K_{\parallel})$ is the paramagnetic anisotropy and θ and r are the structural parameters as defined by Horrocks (1973). Both these informations are available on the Fe(TPP)X series (Behere *et al* 1982). The dipolar term can therefore be easily calculated for pyrrole, meso and quaternary phenyl carbon atoms, but for the other phenyl carbons slight complication is involved due to the rotation of the phenyl ring in solution, which will affect the evaluation of r and θ . Hence we calculated r and θ at an interval of every 10° by rotating the phenyl ring through $\pm 40^\circ$ with respect to porphyrin plane and used an average value for the calculation of the dipolar terms. The dipolar and contact terms so obtained are included in table 1.

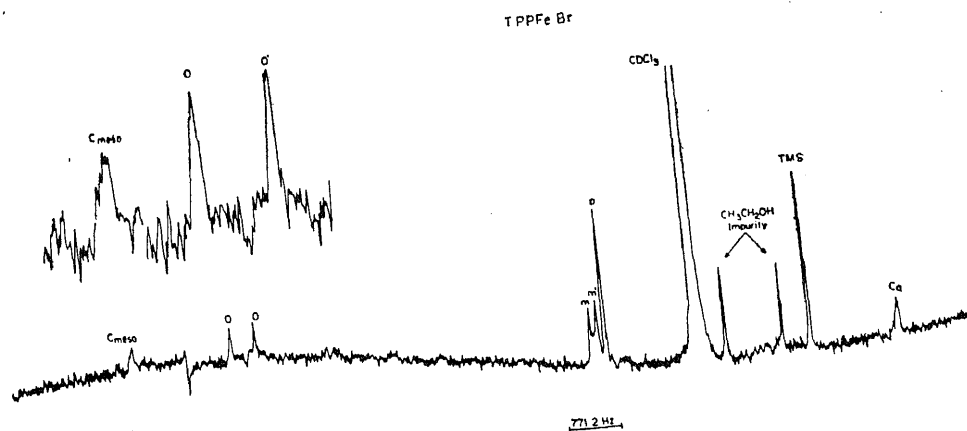


Figure 2. A typical ^{13}C spectrum of Fe(TPP)Br at room temperature. All the carbon resonances are labelled.

Table 1. ^{13}C shifts for $\text{Fe}(\text{TPP})\text{X}$

	$\text{Fe}(\text{TPP})\text{Cl}$				$\text{Fe}(\text{TPP})\text{Br}$				$\text{Fe}(\text{TPP})\text{I}$			
	$\delta_{\text{C}}^{\text{ISO}}$	$\delta_{\text{C}}^{\text{DIP}}$	$\delta_{\text{C}}^{\text{CON}}$	$\delta_{\text{H}}^{\text{CON}}$	$\delta_{\text{C}}^{\text{ISO}}$	$\delta_{\text{C}}^{\text{DIP}}$	$\delta_{\text{C}}^{\text{CON}}$	$\delta_{\text{H}}^{\text{CON}}$	$\delta_{\text{C}}^{\text{ISO}}$	$\delta_{\text{C}}^{\text{DIP}}$	$\delta_{\text{C}}^{\text{CON}}$	
Meso (Cm)	-329.8	-15.8	-314.0	..	-334.7	-32.6	-302.1	..	-311.5	-35.7	-275.8	
Quaternary phenyl (q)	+177.9	-5.2	+183.1	..	+182.6	-11.2	+171.4	..	+177.3	-12.3	+189.6	
Ortho (o)	-260.1	-2.7	-257.4	..	-272.1	-5.8	-266.3	+5.0	-278.1	-7.5	-270.6	
Ortho (o')	-246.1	-2.2	-243.9	..	-255.1	-5.2	-249.9	+5.20	-255.1	-6.2	-248.1	
Meta (m)	-22.9	-1.6	-21.3	-4.10	-25.0	-3.8	-21.2	-3.25	-27.0	-4.1	-22.9	
Meta (m')	-19.3	-1.3	-18.0	-3.24	-20.5	-2.4	-18.1	-2.83	-20.8	-3.6	-17.2	
Para (p)	-13.3	-1.3	-12.0	+2.35	-14.6	-3.0	-11.6	+3.06	-15.8	-3.3	-12.5	

The shifts are relative to TMS and corrected for diamagnetism (see text). All negative shifts are 'down-field' with respect to TMS.

4. Discussion

Table 1 shows several interesting results. As expected ^{13}C shifts are much larger than the corresponding proton shifts. This is true not only for pyrrole but for phenyl carbon shifts as well. In view of the large shifts, the dipolar contributions which lie in the range of 1-40 ppm appear insignificant. This is an encouraging result as it allows the neglect of dipolar contribution for the analysis of ^{13}C shifts. This is contrary to the situation for proton NMR where the dipolar contribution plays a significant role in the interpretation of the data (Mitra 1977 ; Behere *et al* 1982).

The variation in the ^{13}C shifts across the $\text{Fe}(\text{TPP})\text{X}$ does not show any definite trend, though the systematic decrease in the meso-carbon shift from chloride to the iodide complex appears to be real. It is interesting that a very recent theoretical calculation on five coordinated high spin iron(III) porphyrin predicts just a similar variation in the meso-carbon shift (Mun *et al* 1981). Nevertheless the effect of variation in the axial ligand on the ^{13}C shift of the basal porphyrin ring is small and for most cases difficult to discern.

We shall now discuss the spin delocalisation mechanisms responsible for the observed contact shifts of the various carbons and protons in this series. We observe from table 1 that the meso-carbon shows a large down-field shift while the phenyl quaternary carbon bonded to it is considerably up-field shifted. The shift pattern of the phenyl ortho, meta and para carbons and protons is quite interesting. The ^{13}C shifts for these nuclei show a sharp decrease in magnitude in going from ortho to meta to para but the sign of the shift remains the same. This is in contrast to the situation for the corresponding proton shifts which show alternation in sign but no attenuation.

The ferric ion in the $\text{Fe}(\text{TPP})\text{X}$ series has unpaired electrons in all the five d -orbitals of π and σ symmetry. The unpaired electrons can therefore delocalise over the porphyrin ring through its π and σ molecular orbitals. It has recently been shown that the meso-carbon shift arises mainly through the unpaired spin-density in the π molecular orbitals (Mispelter *et al* 1981). This unpaired spin-density in the π -MO can induce an unpaired spin density at the phenyl quaternary carbon either through π - σ correlation (Carrington and McLachlan 1967 ; LaMar 1973) or through direct p_{π} - σ_{π} interaction (LaMar 1973). The latter contribution is expected to be small because of the orientation of the phenyl rings. Nevertheless both these mechanisms will induce at the phenyl quaternary carbon a spin density opposite in sign to that at the meso-carbon, as is experimentally observed. The unpaired spin density induced at the phenyl quaternary carbon in both σ and π MO propagates over the phenyl rings. The proton contact shifts found earlier (Behere *et al* 1982) are consistent with the spin delocalisation in predominantly π -MO of the phenyl rings. The ^{13}C contact shifts of the phenyl carbons however show typical variation expected of σ -delocalisation resulting from the unpaired spin density in the σ -atomic orbitals of these carbon atoms. While these simple arguments explain qualitatively the unpaired spin density at various carbon sites, a quantitative description may be much more complicated (Carrington and McLachlan 1967).

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Study of mixed complexes by polarography : cadmium-glycine-methionine and cadmium-glycine-ethylenediamine complexes

M RAMAIAH[†], B G BHAT* and R SUNDARESAN^{††}

Chemistry Department, Indian Institute of Technology, Powai, Bombay 400 076, India

[†] Present address : Chemistry Department, Regional Engineering College, Warangal 506 004, India

^{††} Analytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India

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Abstract. The mixed complexes of cadmium with glycine and methionine and glycine and ethylenediamine have been studied by polarography and the stability constants of the various species formed have been evaluated.

Keywords. Mixed complexes ; cadmium ; glycine ; methionine ; ethylenediamine ; polarography.

1. Introduction

Though Schaap and McMasters (1961) pioneered the extension of the polarographic method of DeFord and Hume (1951) to the study of mixed complexes, not much work has since been reported in the literature. This paper presents a polarographic study of the mixed complexes of cadmium with glycine-methionine and glycine-ethylenediamine.

2. Experimental

Glycine (E Merck, pro analysi) and DL-methionine (E Merck, LR) were used without purification. Ethylenediamine (E Merck, LR) was standardised against hydrochloric acid using methyl orange as the indicator. A stock solution of cadmium was prepared from cadmium sulphate (E Merck, GR) and standardised with EDTA. Potassium nitrate, used as the supporting electrolyte, was of BDH AnalaR grade. The solutions were made in double distilled water and pH was measured with a Philips pH-meter (pp-9040). Polarograms were taken on a manual set-up using a H-cell with an agar plug and a saturated calomel electrode (SCE) served as the reference electrode. Currents are reported after correcting for the residual currents. Correction for the IR drop in the potentials was not necessary.

* To whom correspondence should be made.

separately in 1.0 M potassium nitrate at different pH. The electrode reaction was reversible in both the cases. The glycinate [G] and the methioninate [Me] concentrations were calculated from the pH of the solution and the pK_a of the ligands determined as 9.76 for glycine and 9.10 for methionine. The half-wave potentials were measured as a function of $\log [G]$ or $\log [Me]$ from which the stability constants were calculated as $\log \beta_3 = 9.40$ for cadmium-glycine and $\log \beta_1 = 3.80$, $\log \beta_2 = 6.35$ and $\log \beta_3 = 8.19$ for cadmium-methionine systems by the methods of Lingane (1941) and DeFord and Hume (1951) respectively

In the investigation of cadmium-glycine-methionine system three series of measurements were made under the same experimental conditions as for the 'simple' systems, keeping [Me] constant and varying [G]. The polarograms were well defined and the reduction was reversible. The half-wave potentials (table 1) were used to calculate a function, F_{00} , using the relationship (Schaap and McMasters 1961)

$$F_{00}(\text{Me}, G) = \text{antilog} [0.4343 nF/RT \{E_{1/2(s)} - E_{1/2(o)}\} + \log \{i_a(s)/i_a(o)\}] \quad (1)$$

where the symbols have the usual meaning. This may be written, at constant methioninate concentration, as

$$F_{00}(\text{Me}, G) = A + B[G] + C[G]^2 + D[G]^3 \quad (2)$$

where

$$\left. \begin{aligned} A &= [1 + \beta_{\text{Me}_2\text{G}_0} [\text{Me}] + \beta_{\text{MeG}_2\text{O}} [\text{Me}]^2 + \beta_{\text{Me}_3\text{G}_0} [\text{Me}]^3] \\ &= [1 + \beta_{10} [\text{Me}] + \beta_{20} [\text{Me}]^2 + \beta_{30} [\text{Me}]^3], \\ B &= [\beta_{\text{Me}_2\text{G}_1} + \beta_{\text{Me}_1\text{G}_1} [\text{Me}] + \beta_{\text{Me}_2\text{G}_1} [\text{Me}]^2] \\ &= [\beta_{01} + \beta_{11} [\text{Me}] + \beta_{21} [\text{Me}]^2], \\ C &= [\beta_{\text{Me}_2\text{G}_2} + \beta_{\text{Me}_1\text{G}_2} [\text{Me}]] \\ &= [\beta_{02} + \beta_{12} [\text{Me}]] \text{ and} \\ D &= \beta_{\text{Me}_3\text{G}_3} = \beta_{03}. \end{aligned} \right\} \quad (3)$$

$\beta_{\text{Me}_2\text{G}_y}$ refer to the stability constants of the mixed complex species $\text{Cd Me}_2\text{G}_y$. The constants A , B , C and D , evaluated by a graphical procedure, are reported in table 1.

The values of A agreed with the calculated values based on the stability constants obtained from the 'simple' system. β_{11} and β_{21} were calculated from the values of B using (3) as 1.0×10^6 and 1.26×10^9 respectively. Similarly β_{02} and β_{12} were determined from C as 3.98×10^7 and 3.16×10^9 respectively. The average value of D corresponds to β_{03} and agreed with that obtained from cadmium-glycine system.

The relative stability of a mixed complex over the parent binary complex and the compatibility between the ligands, indicated by the "mixing constant" k_{M}

$\text{sec}^{-1/2}$; $E_{1/2(s)} = -0.580 \text{ V vs SCE}$; $i_{d(s)} = 2.35 \mu\text{A}$; $i_{d(e)}_{\text{mean}} = 2.00 \mu\text{A}$.

$[G] \times 10^3$ [M]	$E_{1/2}$ - V vs SCE	$F_{00} \times 10^{-4}$	$F_{10} \times 10^{-6}$	$F_{20} \times 10^{-8}$
--------------------------	-------------------------	-------------------------	-------------------------	-------------------------

$$[M] = 3.58 \times 10^{-3} \text{ M}$$

1.42	0.701	1.25	1.74	0.66
2.84	0.705	1.69	2.43	2.75
5.67	0.710	2.49	2.62	1.71
9.93	0.717	4.25	3.27	1.63
14.19	0.725	7.84	4.82	2.24
21.29	0.733	13.94	6.08	2.08
28.37	0.738	21.24	7.13	1.93
42.57	0.743	31.15	7.08	1.28
56.74	0.759	106.1	18.53	2.97

$$A = 1.00 \times 10^4; B = 1.65 \times 10^6; C = 1.55 \times 10^8; D = 2.30 \times 10^9.$$

$$[Me] = 7.15 \times 10^{-3} \text{ M}$$

1.42	0.725	7.74	5.25	..
2.84	0.727	9.03	7.14	3.32
5.67	0.729	11.36	7.68	2.61
9.93	0.735	17.31	10.38	4.21
14.19	0.738	20.97	9.84	2.57
21.29	0.745	37.25	14.21	3.76
28.37	0.749	50.60	15.37	3.23
42.57	0.759	108.9	23.93	4.16
56.74	0.764	159.7	26.91	3.65

$$A = 7.00 \times 10^4; B = 6.20 \times 10^6; C = 2.75 \times 10^8; D = 2.20 \times 10^9.$$

$$[Me] = 0.107 \text{ M}$$

1.42	0.739	22.93	10.07	..
2.84	0.739	22.93	5.04	..
5.67	0.743	31.16	17.04	3.93
9.93	0.746	39.12	17.83	3.05
14.19	0.749	47.48	18.31	2.47
21.29	0.754	72.37	23.89	4.27
28.37	0.760	110.3	31.30	5.82
42.57	0.765	168.1	34.44	4.61
56.74	0.772	287.4	46.86	5.65

$$A = 2.15 \times 10^5; B = 1.48 \times 10^7; C = 3.75 \times 10^8; D = 2.70 \times 10^9.$$

and the enhanced (or sometimes decreased) stability due to factors other than statistical, given by the "stabilisation constant" k_s , are calculated from the expressions (Marcus and Eliezer 1962)

$$k_{M(x,y)} = \beta_{xy} \cdot \beta_{m,0}^{-x/m} \cdot \beta_{0,m}^{-y/m}, \quad (x + y = m), \quad (4)$$

$$\text{and} \quad \log k_s = \log k_M - \log (m! / x! y!). \quad (5)$$

The values of k_M and k_s for this system, calculated in this manner, are given in table 2.

3.2. Cadmium-glycine-ethylenediamine complexes

A preliminary investigation of cadmium-ethylenediamine complexes in 1.0 M potassium nitrate indicated reversible reduction. The dissociation constant, pK_2 of ethylenediamine was determined as 10.10 and the stability constant β_3 was calculated from the half-wave potential data as $10^{11.98}$. In the study of cadmium-glycine-ethylenediamine system, three sets of data were obtained at three concentrations of glycine, varying that of ethylenediamine. The reduction was reversible and the half-wave potential data (not presented here for the sake of brevity) were solved for the stability constants of the various complex species as discussed earlier. These values as well as $\log k_M$ and $\log k_s$ are given in table 2.

Table 2. Stability constants and $\log k_M$ and $\log k_s$ values.

Complex species	$\log \beta$		$\log k_M$	$\log k_s$
	Present work	Literature values	Present work	
Cd (Me)	3.80	3.81	..	..
Cd(Me) ₂	6.35	6.24	..	..
Cd(Me) ₃	8.19	8.32	..	..
Cd(G)	..	4.54	..	..
Cd(G) ₂	7.60	8.08	..	..
Cd(G) ₃	9.40	9.78	..	..
Cd(Me) G	6.00	..	-0.98	-1.28
Cd(Me) ₂ G	9.10	..	+0.51	+0.03
Cd(Me) G ₂	9.50	..	+0.52	+0.02
Cd(En)	..	5.60	..	..
Cd(En) ₂	..	10.63	..	..
Cd(En) ₃	11.98	12.10	..	..
Cd(En) G	9.11	..	-0.01	-0.31
Cd(En) G ₂	11.23	..	+0.97	+0.50

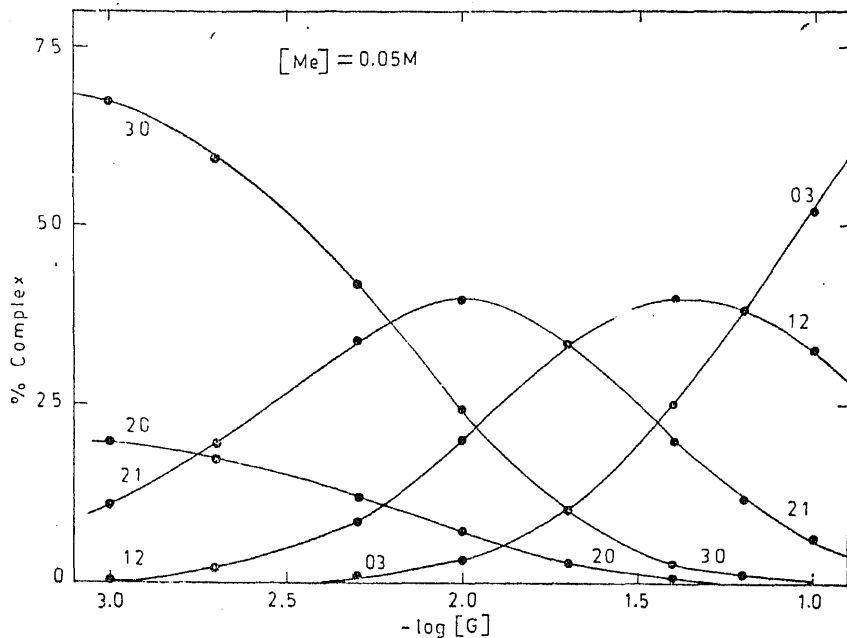


Figure 1. Distribution of cadmium as complexes.

Table 3. Complex equilibria and equilibrium constants.

Equilibria	log K
$Cd + Me + G \rightleftharpoons Cd(Me)(G)$	6.00
$Cd + 2Me + G \rightleftharpoons Cd(Me)_2(G)$	9.10
$Cd + Me + 2G \rightleftharpoons Cd(Me)(G)_2$	9.50
$Cd(Me)(G) + G \rightleftharpoons Cd(Me)(G)_2$	3.50
$Cd(Me)(G) + Me \rightleftharpoons Cd(Me)_2(G)$	3.10
$Cd(Me)_2(G) + G \rightleftharpoons Cd(Me)(G)_2 + Me$	0.40
$Cd(G)_2 + Me \rightleftharpoons Cd(Me)(G)_2$	1.90
$Cd(Me) + G \rightleftharpoons Cd(Me)(G)$	2.20
$Cd(Me)_2 + G \rightleftharpoons Cd(Me)(G) + Me$	-0.35
$Cd(Me)_3 + G \rightleftharpoons Cd(Me)_2(G) + Me$	0.91
$Cd(Me)(G)_2 + G \rightleftharpoons Cd(G)_3 + Me$	-0.10
$Cd + En + G \rightleftharpoons Cd(En)(G)$	9.11
$Cd + En + 2G \rightleftharpoons Cd(En)(G)_2$	11.23
$Cd + 2En + G \rightleftharpoons Cd(En)_2(G)$	12.02
$Cd(En)(G) + En \rightleftharpoons Cd(En)_2(G)$	2.91
$Cd(En)(G) + G \rightleftharpoons Cd(En)(G)_2$	2.12
$Cd(En)(G)_2 + En \rightleftharpoons Cd(En)_2(G) + G$	0.79
$Cd(G)_2 + En \rightleftharpoons Cd(En)(G) + G$	1.51
$Cd(G)_3 + En \rightleftharpoons Cd(En)(G)_2 + G$	1.83

It is seen from table 2 that $\log k_M$ for the 1, 2 and 2, 1 complexes of both the systems are positive indicating the compatibility between the ligands. Glycine is more compatible with ethylenediamine probably because the chelating power of ethylenediamine is more due to the presence of two nitrogen donors. The co-ordination unsaturated 1, 1 is 'not important' in both the systems as inferred from the negative values of $\log k_s$ and $\log k_M$. It is, therefore, apparent that the species present in solution in the concentration ranges studied are mostly 20, 30, 21, 12 and 03 complexes. The distribution of cadmium as these complex species at $[Me] = 0.05$ M is depicted in figure 1 as a function of glycinate concentration as an example. The equilibria between the different complex species are given in table 3 from which the facility with which a ligand adds on to or substitutes another ligand may be deduced.

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***In vitro* antimicrobial-activity studies on the mixed ligand complexes of Hg(II) with 8-hydroxyquinoline and salicylic acids**

Y ANJANEYULU[†], R PRABHAKAR RAO, R Y SWAMY,
A EKNATH* and K NARASIMHA RAO*

Department of Chemistry, Nagarjuna University, Nagarjunanagar 522 510, India

* Government Medical College, Guntur 522 004, India

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Abstract. A series of mixed ligand complexes of Hg(II) with the general formula Hg (OX) (SA) (where OX : 8-hydroxyquinoline, SA : salicylic, 5-chloro-, 3,5-dibromo, 3,5-diiodo, 3,5-dinitro, acetyl thiosalicylic acids) are isolated in pure state and characterised by elemental analysis and infrared data. The low molar conductance of the complexes in dimethylformamide indicates non-electrolyte nature. The antimicrobial activity of these complexes against various bacteria and fungi is studied which indicates that in several cases, the mixed ligand complexes possess fairly highly antimicrobial activity than the binary mercury-oxinate. The lipophilic tendency of these complexes and its influence on the antimicrobial activity is critically examined. A probable mechanism for the toxic action of these complexes against various organisms is discussed.

Keywords. Antimicrobial activity ; mixed ligand complexes of Hg(II) ; 8-hydroxyquinoline and salicylic acids.

1. Introduction

Though 8-hydroxyquinoline (oxine) and its divalent metal chelates are known to possess fungicidal and bactericidal properties, the high cost of 8-hydroxyquinoline limits their applicability. Albert *et al* (1953) explained the antimicrobial activity of copper-oxinate assuming that the *bis*-chelate due to its high liposolubility penetrates the cell, reaches the site of action and there it undergoes dissociation into 1 : 1 complex and free 8-hydroxyquinoline. The 1 : 1 charged complex thus formed will become the toxic entity by combining with and blocking the metal-binding sites on enzymes. The same mechanism may equally apply well for explaining the antimicrobial activity of all divalent metal oxinates.

It has been observed that the cost factor can be minimised by replacing one oxine molecule in the divalent metal oxinates with low cost fungicides like salicylic

hetero ligands. The results of our study on the mixed ligand complexes of Hg(II) with 8-hydroxyquinoline and salicylic acids are presented in this paper.

2. Experimental

All the chemicals used are analytical grade (BDH) reagents.

2.1. General method for the preparation of the complex

Equimolar solutions of salicylic acid or substituted salicylic acids (0.2 M), 8-hydroxyquinoline (0.2 M) and Hg(II) acetate (0.2 M) in 80% aqueous methanol are mixed. After stirring for half an hour, the product is removed by filtration, washed with several volumes of water and boiled in acetone and filtered. The complexes are dried at 70°C for 12 hr. Metal and nitrogen are estimated by standard methods.

2.2. Physical measurements

Infrared spectra are recorded by using Perkin Elmer model 577 spectrophotometer (4000 cm^{-1} to 200 cm^{-1}) by KBr disc technique. The conductivity of the complexes in DMF (10^{-3} M) is measured at 27°C by systronics conductivity bridge 305.

2.3. Antimicrobial activity

The antimicrobial activity of the compounds in dimethyl formamide (DMF) are examined *in vitro* by serial dilution method (Schaub *et al* 1958) against various bacteria and by paper disc method (Jasper *et al* 1958) against fungi. All the stock cultures were supplied by the Department of Microbiology, All India Institute of Medical Sciences, New Delhi, India. Peptone water and saline water is used for making the inoculum for bacteria (18 hr culture) and fungi respectively. Nutrient broth and Saboround's dextrose agar (M/s. Hindustan Dehydrated Media, Bombay) are used as test media for bacteria and fungi respectively. The minimum inhibition concentration (MIC $\mu\text{g/ml}$) of the compounds against bacteria and average zone of inhibition (mm) of the compounds at 1000 $\mu\text{g/ml}$ against fungi is given in tables 2 and 3. All the tests are carried out in duplicate.

3. Results and discussion

With $5d^{10}$ configuration Hg(II) forms tetrahedral complexes using $6s\ 6p^3$ hybrid orbitals for bonding leaving a completely non-bonding shell ($d_{xy}^4\ d_{z^2}^6$) which can cause least perturbation to preferred stereochemistry. The elemental analyses of these complexes (table 1) show that Hg(II) forms mixed ligand complexes which can be represented as shown below (figure 1).

Table 1. Analytical, conductometric and IR data of the mercury complexes with 8-hydroxyquinoline and substituted salicylic acids.

Compound	Decomp. temp. °C	Colour	Found (calculated)%		Molar conductance (in Mho ⁻¹ cm ² /g)	IR freq encies (cm ⁻¹) in mixed liand complexes			
						Oxine		Salicylic acids	
			Metal	Nitrogen		ν (C-O)	ν (M-O)	ν (M-N)	ν (O-C-O) asy. sy.
Hg (OX) (SA)	193	yellow	41.30 (41.63)	2.86 (2.91)	3.0	1110 (b)	390 (w)	540 (b)	1580 (b) 1460 (s)
Hg (OX) (Cl-SA)	192	yellow	38.62 (38.85)	2.63 (2.71)	2.4	1110 (b)	390 (w)	540 (w)	1580 (b) 1470 (b)
Hg (OX) (2Br-SA)	232	yellow	31.20 (31.36)	2.10 (2.19)	4.0	1110 (s)	390 (w)	560 (b)	1570 (w) 1480 (s)
Hg (OX) (2I-SA)	190	orange yellow	27.01 (27.36)	1.82 (1.91)	3.7	1110 (s)	390 (w)	550 (w)	1580 (b) 1460 (s)
Hg (OX) (2NO ₂ -SA)	198	yellow	34.93 (35.00)	7.24 (7.34)	3.2	1110 (s)	390 (w)	540 (w)	1580 (s) 1460 (s)
Hg (OX) (Ace-SA)	201	yellow	38.18 (38.29)	2.58 (2.67)	4.5	1110 (s)	390 (w)	540 (w)	1580 (s) 1460 (s)
Hg (OX) (Thio-SA)	205	white	41.54 (41.63)	2.83 (2.93)	2.1	1110 (s)	400 (w)	540 (b)	1580 (s) 1460 (s)

8-hydroxyquinoline; (SA) : salicylic acid; (Cl-SA) : 5-chlorosalicylic acid ; (2Br-SA) : 3,5-dibromosalicylic acid; (2NO₂-SA) : 3,5-dinitrosalicylic acid; (2I-SA) : 3,5-diiodosalicylic acid ; (Ace-SA) : Acetyl salicylic acid ; (Thio-SA) : thiosalicylic acid ; (s) : sharp ; (w) : weak ; (b) : broad.

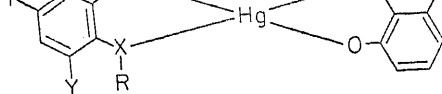
Table 2. Antibacterial activity MIC ($\mu\text{g/ml}$) of mercury complexes with 8-hydroxy-quinoline and substituted salicylic acids at 37°C after 18 hours in nutrient broth.

Sl. No.	Compound	Gram-positive		Gram-negative							
		1	2	3	4	5	6	7	8	9	10
1.	Hg (OX) ₂	3.1	50	25	50	50	50	25	100	12.5	25
2.	Hg (OX) (SA)	6.2	50	25	50	50	50	25	50	25	25
3.	Hg (OX) (Cl-SA)	12.5	50	3.1	12.5	6.2	100	12.5	100	12.5	50
4.	Hg (OX) (2Br-SA)	50	12.5	12.5	12.5	25	100	25	50	25	25
5.	Hg (OX) (2I-SA)	100	50	100	100	100	>100	>100	>100	>100	>100
6.	Hg (OX) (2NO ₂ -SA)	100	100	25	12.5	25	100	25	100	25	50
7.	Hg (OX) (Ac-SA)	6.2	12.5	12.5	3.1	6.2	25	12.5	50	12.5	12.5
8.	Hg (OX) (Thio-SA)	50	12.5	6.2	6.2	12.5	100	12.5	100	6.2	6.2

(1) *Staphylococcus albus*, (2) *Staphylococcus aureus*, (3) *Shigella schmitzi*, (4) *Pseudomonas pyogenes*, (5) *Shigella sonnei*, (6) *Klebsilla aerogenes*, (7) *Shigella flexneri*, (8) *Vibriacholerae*, (9) *Salmonella typhi*, (10) *Salmonella paratyphi-B*.

Table 3. Antifungal activity of the mercury complexes with 8-hydroxyquinoline and substituted salicylic acids at 1000 $\mu\text{g/ml}$ after 48 hours at 30°C .

Sl. No.	Compound	Zone of inhibitions at 1000 $\mu\text{g/ml}$ in mm					
		Fungi	1	2	3	4	5
1.	Hg (OX) ₂		10	9	9	10	8
2.	Hg (OX) (SA)		9	8	10	10	12
3.	Hg (OX) (Cl-SA)		8	10	9	9	10
4.	Hg (OX) (2Br-SA)		7	12	..	9	9
5.	Hg (OX) (2I-SA)		8	7	10	8	8
6.	Hg (OX) (2NO ₂ -SA)		8	9	8	8	12
7.	Hg (OX) (Ac-SA)		8	..	..	9	11
8.	Hg (OX) (Thio-SA)		..	..	..	..	7



Y = Cl, Br, NO₂, I, H

X = O or S

R = H or COCH₃

The low molar conductance values of these complexes in DMF indicate that they are of non-electrolyte type.

3.1. IR data

The important absorption peaks of the IR spectra of these complexes agree with their structure. In all the mixed ligand complexes the symmetric and asymmetric vibrations of (O-C-O) group (Bellamy 1956) of salicylic acids are observed at $\sim 1420\text{ cm}^{-1}$ and $\sim 1570\text{ cm}^{-1}$ respectively, while the carbonyl stretching frequency which appeared in the free salicylic acids between $1650\text{--}1670\text{ cm}^{-1}$ disappeared. This clearly indicates metal-carboxylate linkage. Charles *et al* (1956) reported that in several 8-hydroxyquinoline complexes of divalent metals, the $\nu_{(\text{C-O})}$ appeared at $\sim 1120\text{ cm}^{-1}$ region and the position of the band slightly varies with the metal. The $\nu_{(\text{C-O})}$ which appeared in the free oxine molecule at 1090 cm^{-1} is found to be shifted in all the mixed complexes giving a strong absorption band at 1110 cm^{-1} which clearly indicates the coordination of 8-hydroxyquinoline in the complexes. In all the mixed ligand complexes, the observed sharp peaks between $\sim 540\text{--}560\text{ cm}^{-1}$ and $\sim 340\text{--}400\text{ cm}^{-1}$ may be assigned to the M-N and M-O stretching frequencies respectively (Nakamoto 1970).

3.2. Antimicrobial activity

In many cases the toxic effect of the mercury-oxine-salicylic or substituted salicylic acid mixed ligand complexes against various bacteria and fungi is found to be either equal or slightly greater when compared to the *bis* (8-hydroxyquinolinato) mercury(II) complex. Salicylic acid or substituted salicylic acids and their mercury chelates are found to have measurable activity against these bacteria and fungi at relatively very high concentrations (for bacteria $> 100\text{ }\mu\text{g/ml}$, fungi $> 2000\text{ }\mu\text{g/ml}$). This may be due to their higher water solubility.

In explaining the antimicrobial activity of *bis* (8-hydroxyquinolinato) copper(II), Albert *et al* (1953) believed that the 1 : 2 chelate due to its liposolubility is necessary to transport the toxic moiety, i.e., 1 : 1 chelate to the site of action. The assumption was supported by the fact that antimicrobial activity of these complexes was reversed in the presence of excess of copper. This may be due to the inability of the ionically charged 1 : 1 chelate (which is produced in the presence of excess of metal) to penetrate the cell membrane. Block (1955) proposed that the natural chelators within the cell were poisoned by removing copper from Cu(II)-oxine,

copper and 8-hydroxyquinoline remove the copper and form lipid-soluble chelates. Esposito and Fletcher (1961) proposed that the activity of copper(II)-8-hydroxyquinoline was due to the 1 : 1 complex which could bind with an enzyme site that was involved in the biosynthesis of pteridines. This was based on the reversal of inhibition by several pteridines and precursors. It was also believed that a similar mechanism may be working well in explaining the toxic action of all other bivalent oxinates.

According to Overton's concept of cell permeability the lipid membrane surrounding the cell favours the passage through that membrane of lipid-soluble materials and liposolubility is considered as one of the important factors which control the antimicrobial activity of any toxic agent. The partition of the toxic agent between oily alcohol or chloroform and 7.4 pH phosphate buffer (pH of the biological medium) system is considered as a good model to understand the lipophobic or lipophilic tendency (Dwyer and Mellor 1964). So we have determined distribution of all these complexes in between chloroform and 7.4 pH buffer and the results are given in table 4. As expected the mercury-oxine-salicylic or substituted salicylic acid mixed complexes have lower partition coefficient in chloroform when compared to the binary mercury oxinate. However, in

Table 4. Percentage of extraction of metal into chloroform at 7.4 pH.

Sl. No.	Complex	% of mercury extracted into chloroform
1.	Hg (OX) ₂	80
2.	Hg (SA) (OX)	23
3.	Hg (Cl-SA) (OX)	28
4.	Hg (2Br-SA) (OX)	76
5.	Hg (2I-SA) (OX)	38
6.	Hg (2NO ₂ -SA) (OX)	34
7.	Hg (Acc-SA) (OX)	44
8.	Hg (Thio-SA) (OX)	62

The extraction of mercury(II) with various salicylic acids into chloroform are found to be less than 20% at 7.4 pH.

many cases the mixed complexes have equal or slightly more toxic effect against various bacteria and fungi in comparison with binary complex. This indicates that in the mixed complexes not only the 1 : 1 mercury-oxine complex is acting as toxic agent but also the released salicylic acid may be playing an important role in the antimicrobial activity through a different mechanism. The salicylic acids or mercury salicylate chelates, though possess toxic effect, due to their higher water solubility cannot go to the site of action as much as the mixed complexes can penetrate. If in the mixed complexes also the 1 : 1 mercury-oxine is the only toxic moiety then the antimicrobial activity of the mixed complexes should increase with increasing pK_1 values of the salicylic acids and mercury-oxine-diiodosalicylic acid must have maximum activity. But no such relation is found to exist from their antimicrobial activity screening studies (tables 2 and 3). It is also believed that if the geometry and charge distribution around the molecules are incompatible with geometry and charge distribution around the pores of the fungal or bacterial cell wall, penetration through the wall by the toxic agent cannot take place and toxic reactions within the spore do not occur. This may be one of the reasons for certain mixed ligand complexes showing less effective antimicrobial activity than the corresponding $Hg(OX_2)$ complex.

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Synthesis and structural studies on Ni(II) chloride complexes of N'-(substituted) formamidino-N'-(substituted) carbamides and thiocarbamides

K L MADHOK

Centre for Rural Development and Appropriate Technology, Indian Institute of Technology, Delhi Hauz Khas, New Delhi 110 016, India

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Abstract. Nickel(II) chloride reacts with N,N'-diarylformamidino-N"-arylcabamides, thiocarbamides and N-benzoylformamidino-N"-arylcabamides, thiocarbamides forming complexes of the general formula $[\text{Ni} (\text{Ar.NH.C} (\text{NH}) \text{NH.C.X. NH.R})_2] \text{Cl}_2$ (R = phenyl, orthotolyl and paratolyl ; Ar = benzoyl ; X = S, O) and $[\text{Ni} (\text{R.NH.C.X.NH.C} (\text{N.Ph.})\text{NH.Ph.})_2] \text{Cl}_2$ (R = phenyl, orthotolyl, paratolyl ; Ph = phenyl ; X = S, O). The ligands when oxidized with iodine undergo ring closure to related 3,5-diaryl-amino 1,2,4-thiadiazolidines and 3,5-diaryl-amino-1,2,4-diazolidines, while the complexes are not susceptible to oxidation. This confirms the binding in complexes is through sulphur and oxygen of the ligands.

Keywords. Nickel(II) chloride complexes ; potentiometric oxidations ; 3,5-diaryl-amino-1,2,4-thiadiazolidines ; 3,5-diaryl-amino-1,2,4-diazolidines.

Introduction

Metal complexes of sulphur donor ligands have received great attention during recent years (Horsfall and Rich 1951) because of their versatile use as antifungal and antibacterial agents. A survey of literature reveals that compounds containing both C=O and C=S groups possess significant fungicidal activity (Horsfall and Rich 1951). Despite the fact that a variety of sulphur donor ligands have been studied (Akbar Ali and Livingstone 1974 ; Mishra 1980 ; Srivastava and Madhok 1978 ; Madhok and Srivastava 1980), for the synthesis of metal complexes it appears that N,N'-(substituted) formamidino-N"- (substituted) carbamides (SFSC) and N,N'-(substituted) formamidino-N"- (substituted) thiocarbamides (SFSTC) having both C=O and C=S with =NH groups, has not been used. As a continuation of our earlier work (Srivastava and Madhok 1978 ; Madhok and Srivastava 1980) on metal chelates of substituted thioureas, thiobiurets, the present paper describes the studies of Ni(II) chloride complexes of the title ligands.

Experimental

The ligands N,N'-diphenylformamidino N'-phenylthiocarbamido (DPFPC), N,N'-diphenylformamidino N'-phenylthiocarbamido (DPFPTC), N,N'-diphenylformamidino N'-orthotolylthiocarbamido (DPF.o.TTC), N,N'-diphenylformamidino N'-paratolylthiocarbamido (DPF.p.TTC), N-benzoylformamidino N'-phenylthiocarbamido (BFPC), N-benzoylformamidino N'-phenylthiocarbamido (BFPTC), N-benzoylformamidino N'-orthotolylthiocarbamido (BF.o.TTC) and N-benzoylformamidino N'-paratolylthiocarbamido (BF.p.TTC) were prepared by the method as described earlier (Srivastava and Madhok 1978). The purity of ligands was checked by sharp melting point and elemental analysis.

2.1. General method of the preparation of complexes

Standard alcoholic solution (0.1 M) of nickel chloride (200 ml) was mixed together with 200 ml of (0.2 M) alcoholic solution of the ligands and refluxed at 70°C for about 2 hr. It was then allowed to cool during which a silver grey precipitate was obtained which was analysed after being dried *in vacuo*. Melting points of these complexes were determined in open capillary tubes on a unimelt temperature apparatus and are uncorrected. In all the complexes, nickel was estimated as dimethylglyoximate nickel(II). Sulphur and chlorine were estimated by standard methods (Clarke 1960; Erdy 1965). The analytical results are recorded in table 1.

Table 1. Analytical results of Ni(II) chloride complexes.

Compound	% Ni found (calc.)	% Cl found (calc.)	% S found (calc.)	Molar conductance	
				Molarity (M)	Conductance cm ² mol ⁻¹ Ω ⁻¹
[Ni (DPFPTC) ₂] Cl ₂	7.153 (7.134)	8.662 (8.642)	7.692 (7.789)	0.10 × 10 ⁻³	150
[Ni (DPFPC) ₂] Cl ₂	7.399 (7.432)	8.980 (8.991)		0.10 × 10 ⁻³	148
[Ni (DPF.o.TTC) ₂] Cl ₂	6.955 (6.907)	8.420 (8.356)	7.555 (7.532)	0.12 × 10 ⁻³	152
[Ni (DPF.p.TTC) ₂] Cl ₂	6.955 (6.907)	8.486 (8.356)	7.700 (7.532)	0.11 × 10 ⁻³	158
[Ni (BFPTC) ₂] Cl ₂	8.100 (8.089)	9.820 (9.786)	11.155 (11.100)	0.12 × 10 ⁻³	160
[Ni (BFPC) ₂] Cl ₂	8.488 (6.463)	10.300 (10.230)		0.10 × 10 ⁻³	157
[Ni (BF.o.TTC) ₂] Cl ₂	7.890 (7.787)	9.550 (9.421)	8.932 (8.892)	0.11 × 10 ⁻³	149
[Ni (BF.p.TTC) ₂] Cl ₂	7.890 (7.787)	9.550 (9.421)	8.932 (8.892)	0.11 × 10 ⁻³	149

The magnetic susceptibility of the chelates was determined by Gouy's magnetic balance applying a field strength of about 4.5×10^3 gauss. Mercury(II) tetrathiocyanatecobaltate(II) $[\text{Hg Co}(\text{CNS})_4]$ was used as the standard.

The infrared spectra of the ligands and complexes were recorded in KBr pellets in Perkin Elmer grating infrared spectrophotometer model 237-B in the range of $4000\text{--}650\text{ cm}^{-1}$ using the pallet technique. The spectra are complicated and difficult to interpret, however only those peaks that could be assigned with reasonable certainty are listed in table 3.

The solubility of all these complexes is high in dimethylformamide. Thus the conductance measurements were carried out in freshly distilled dimethylformamide solution, on conductivity meter type LBR of Wissenschaftlich Technische, Werkstätten, Germany, with dip type cell. The solutions of the complexes were prepared immediately before use.

Studies on oxidation of ligands and their complexes were carried out with iodine solution in tetrahydrofuran using calomel and platinum electrodes. 20 ml of $M/500$ solution in THF of the ligands and their metal complexes were titrated with $M/50$ iodine solution in THF.

Absorption spectra of Ni(II) chloride complexes were measured by the standard method using Perkin-Elmer UV-VIS spectrophotometer model 139. Ethanol and methanol used were of BDH AnalaR quality and distilled before use. The absorption bands of Ni complexes in ethanol and methanol are represented in table 2. Transition energy E_T was calculated from the relation

$$E_T = \frac{2.859 \times 10^5}{\lambda_{\max} (\text{in } \text{\AA})},$$

and the oscillatory strength f was calculated from the following equation:

$$f = 4.32 \times 10^{-19} \int E dv,$$

utilizing

$$E_{\max} \Delta\bar{\nu} = \int E dv$$

where $\Delta\bar{\nu}$ is the wave number of the half band width. All the data are recorded in table 2.

5. Results and discussion

All the complexes are coloured. Complexes are insoluble in most of the common organic solvents but are soluble in excess of alcohol, tetrahydrofuran and dimethylformamide. All the complexes decomposed on heating above 160°C , complexes are also decomposed by mineral acids.

Magnetic susceptibility of the complexes is found in the range of -0.285 to -0.500×10^{-6} g. The negative susceptibility values are indicative of the diamagnetic nature of the complexes.

The observed values of molar conductance in DMF are in the range of $148\text{--}160$ mhos. The molar conductance results indicate the electrolytic nature of the

Table 2. UV spectral data on ligands and their Ni(II) chloride complexes in ethanol and methanol.

Compound	Ethanol					Methanol				
	Molarity ($\times 10^{-5}$)	$\lambda_{\max}$	$E_{\max}$	E_T (k. cal. mole $^{-1}$)	f	Molarity ($\times 10^{-5}$)	$\lambda_{\max}$	$E_{\max}$	E_T (k. cal. mole $^{-1}$)	
BPTC	9.485	265	85170	107.90	.1375	..	263	81550	107.90	
NiCl $_2$.2BFPTC	..	320	13290	89.35	.2935	9.990	318	12800	89.90	
BFFC	..	265	87540	107.90	.0504	..	250	84010	114.30	
NiCl $_2$.2BFPC	6.172	308	12300	92.81	.1990	3.290	307	11940	93.13	
BF.o.TTC	..	261	91520	109.50	.0810	..	248	83660	115.30	
NiCl $_2$.2BF.o.TTC	9.780	305	12780	93.74	.3639	3.586	305	11570	93.74	
BF.p.TTC	..	263	84450	107.90	.1039	..	257	72830	111.30	
NiCl $_2$.2BF.p.TTC	8.222	320	14180	89.35	.3378	3.364	320	13820	89.35	
DPFPTC	..	246	25020	116.20	.8518	..	245	19890	119.40	
NiCl $_2$.2DPFPTC	4.923	344	26090	83.10	.6415	3.610	342	22590	83.60	
DPFPC	..	247	30100	115.70	1.1820	..	248	26430	115.30	
NiCl $_2$.2DPFPC	5.335	347	28770	82.40	.7450	2.290	345	25780	82.87	
DPF.o.TTC	..	263	31000	108.60	.1250	..	240	27800	119.80	
NiCl $_2$.2DPF.o.TTC	6.545	308	29780	92.81	.2009	2.150	342	26400	83.60	
DPF.p.TTC	..	246	31200	116.20	.1320	..	257	29300	111.30	
NiCl $_2$.2DPF.p.TTC	7.888	347	29800	82.40	.7590	2.000	325	28150	87.96	

Table 3. IR spectral data of ligands and their Ni(II) chloride chelates (in cm^{-1}).

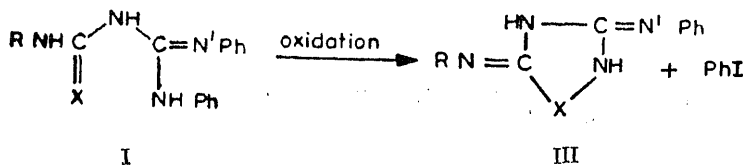
Compound	=NH stretch	C=O stretch	N-H bend	C-H stretch	C-N stretch +N-H bend + (C=S) bend	(C=S) stretch	C=S stretch
PFPTC	3385s	..	1641vw	1540s	1441vw	1225m	729m
$\text{Cl}_2 \cdot 2\text{DPFPTC}$	3280mb	..	1635s	1585s	1485s	1225m	718m
PFPC	3400s	1735w	1440m	1582m	1660m	1260m	..
$\text{Cl}_2 \cdot 2\text{DPFPC}$	..	1720w	1630m	1470w	1422m	1222m	..
PF.o.TTC	3402s	..	1660m	1540m	1430s	1270m	760b
$\text{Cl}_2 \cdot 2\text{DPF.o.TTC}$	..	..	1648s	1552m	1405s	1258m	745m
PF.p.TTC	3400s	..	1600s	1566m	1441m	1220m	756m
$\text{Cl}_2 \cdot 2\text{DPF.p.TTC}$	..	..	1625w	1575m	1460w	1205b	740m
BFPTC	3400s	1700m	1680s	1550s	1413s	1227s	716w
$\text{Cl}_2 \cdot 2\text{BFPTC}$	3310b	1700m	1630s	1595m	1480w	1215m	702m
BFPC	3360s	1725m	1685s	1550m	1440s	1280w	..
$\text{Cl}_2 \cdot 2\text{BFPC}$	..	1710m	1635vw	1590m	1440ms	1255ms	..
BF.o.TTC	3400ms	1698m	1625sb	1525w	1400m	1775w	750m
$\text{Cl}_2 \cdot 2\text{BF.o.TTC}$	3300m	1698m	1605m	1520w	1475w	1150ws	730w
BF.p.TTC	3400s	1700m	1625s	1563s	1440m	1282s	799w
$\text{Cl}_2 \cdot 2\text{BF.p.TTC}$	3270m	1700m	1620m	1570m	1445wb	1266m	778w

=strong, m = medium, b = broad, w = weak.

On an examination of UV spectra of the ligands and complexes in alcohol, it is observed that the absorption band of the ligands (DPFPTC), (DPF.o.TTC, DPF.p.TTC, BFPTC, BF.o.TTC and BF.p.TTC), 240–265 nm in ethanol and methanol has been shifted to 305 to 347 nm in complexes. This shift is attributed to the fact that during the complex formation π^* energy level is longer due to stabilization of the excited state, so the $n-\pi^*$ transition is shifted to lower wavelength, i.e., lower frequency and consequently lower energy. This also accounts for the fact that thiocarbonyl group is acting as donor in the complex formation. In case of DPFPC and BFPC complexes the $\pi-\pi^*$ transitions (247–265 nm) band is shifted to lower wavelength 307 to 347 nm.

From the infrared spectra of the ligands and their metal chelates, it can be seen that the ligands exhibit a C=O stretching band of medium intensity in the region 1698–1735 cm^{-1} which is observed to be stronger than the usual ketone C=O band (Scheinmann 1970). On chelation with metal the carbonyl absorption peak is shifted to lower frequency (15 cm^{-1}) of comparatively low intensity. As there is almost no change in the benzylic carbonyl frequencies on complexation, the benzylic C=O group cannot be considered as a site for coordination. A peak at 1400–1490 cm^{-1} is due to mixed bend of (C–N) stretch, N–H bend and C=S bend. The strong bands at 3355 to 3400 cm^{-1} in the case of disubstituted forma-

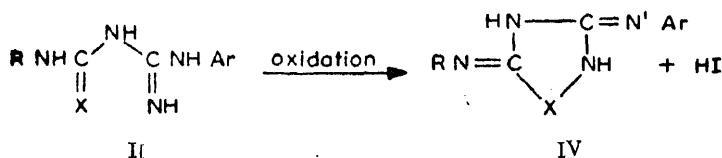
Potentiometric titrations of the ligands indicate that an equal amount of iodine is consumed in the oxidation reaction. It is due to the oxidation of ligands to thiazoles. The interaction of N,N'-diphenyl guanidines or asymmetric guanidines with arylisocyanates and arylisothiocyanates have been shown to afford N,N'-diarylformamidino N''-arylcarbamides and thiocarbamides(I) and N-benzoylformamidino N'-arylcarbamides and thiocarbamides(II). The compounds I and II when oxidized undergo ring closure to III and IV, the related 3,5-diarylamino-1,2,4-diazolidines and 3,5-diaryl-amino-1,2,4-thiadiazolidines (Dixit 1961).



N,N'-diarylformamidino-N''-arylcarbamides,
thiocarbamides

3,5-diaryl-amino-1,2,4-diazolidines and
thiadiazolidines.

Ph = phenyl ; R = phenyl, orthotolyl, paratolyl ; X = O, S



N-benzoylformamidino N'-arylcarbamides,
thiocarbamides.

3,5-diaryl-amino-1,2,4-diazolidines and
thiadiazolidines.

R = C₆H₅CO ; Ar = phenyl, orthotolyl, paratolyl ; X = O, S

On titrating the metal complexes with iodine almost constant values of potential are obtained indicating that the complexes are not being oxidized by iodine. This may be due to the fact that the sulphur and oxygen atoms are already bonded to the metal in the metal chloride complexes and are not free to form the thiols. All these observations show that coordination in the case of DPFP TC, DPF.o. TTC, DPF.p.TTC, BFPTC, BF.o.TTC and BF.p.TTC is through sulphur and nitrogen (of the =NH group) while in the case of BFPC and DPFPC complexes the coordination is through oxygen and nitrogen atoms.

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Synthesis and characterization of copolymers from 4-halo(chloro, bromo) salicylic acid

HASMUKH S PATEL and SHANTI R PATEL

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar 388 120, India

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Abstract. Copolymers have been prepared by condensing a mixture of either 4-chloro or 4-bromosalicylic acid and any one of the comonomer like salicylic acid, *p*-hydroxybenzoic acid, *p*-aminosalicylic acid, *p*-aminobenzoic acid, *p*-cresol and *p*-halo(chloro, bromo)phenol with formaldehyde in the presence of 5 M H₂SO₄. Copolymer composition of each of the copolymer has been estimated on the basis of halogen content and/or on the basis of results of non-aqueous titrations of the copolymer against standard sodium methoxide and/or tetra-*n*-butylammonium hydroxide. The IR spectral characteristics of copolymers have been noted. The viscometric and thermal studies of copolymers have also been carried out.

Keywords. Copolymers from 4-halo(chloro, bromo)salicylic acid.

Introduction

Copolymers from a mixture of salicylic acid and a phenolic or amino derivative of formaldehyde are reported to find many interesting applications (Rozhanovaya and Zasova 1969; Isura Shigeru *et al* 1971; Kimura and Kashiha 1972; Maslyuk and Natanson 1976). Some of the copolymers synthesized from a mixture of resorcinol, formaldehyde and either salicylic acid (Ward *et al* 1975), β -resorcylic acid (DeGeiso *et al* 1963) or *p*-aminosalicylic acid (Dyaltova *et al* 1964) have proved to be specific ion exchangers. Copolymers from salicylic acid, urea and formaldehyde are reported to yield soluble polyelectrolytes (Makhmudov *et al* 1971). In the light of the reports about the promising applications of these copolymers, it was thought that copolymers from a mixture of 4-halo(chloro, bromo)salicylic acid and a phenol or an amine and formaldehyde may possess interesting properties. Hence the work described in the present paper dealing with the synthesis and characterization of such copolymers was undertaken. Out of the two comonomers condensed jointly with formaldehyde one is either 4-chloro (CS) or 4-bromosalicylic acid (BS) and the other comonomer is either salicylic acid (SA), *p*-hydroxybenzoic acid (PHBA), *p*-aminosalicylic acid (PAS), *p*-aminobenzoic acid (PABA), *p*-cresol (PC), *p*-chlorophenol (PCP) or *p*-bromophenol (PBP).

The spectral characteristics of the copolymers have been noted. The viscosity of the copolymers have been measured in DMF and in 80 : 20 (v/v) DMF: water containing 1.0% KBr. Solutions in DMF exhibited polyelectrolyte behaviour in viscometry experiments. The thermal properties of the copolymers have been examined by thermogravimetry.

2. Experimental

Copolymerization of a mixture of 4-chloro (CS) or 4-bromo (BS) salicylic acid and a comonomer [salicylic acid (SA), *p*-hydroxybenzoic acid (PHBA), *p*-aminosalicylic acid (PAS), *p*-amino benzoic acid (PABA), *p*-cresol (PC), *p*-chlorophenol (PCP) or *p*-bromophenol (PBP)] with formaldehyde (F) was carried out in presence of an acid catalyst. In all the syntheses of the copolymers, the molar proportions of CS (or BS), the comonomer and formaldehyde were 1 : 1 : 2 and 5 M H₂SO₄ was used as a catalyst. A typical copolymer synthesis is described here. Other copolymer samples listed in tables 1 and 2 were prepared similarly. However, each copolymer sample was treated typically to free it from the polymer formed by separate condensation of each of the two comonomers with formaldehyde. This treatment is based on the difference in the solubility behaviour of the copolymer and the corresponding homopolymers. The solubility behaviour is summarised in table 1.

Table 1. Solubilities of polymers and copolymers.

Polymer	Copolymer	Solubility in ^a					
		aq. NaHCO ₃	Solvent ether	Acetone	1,4- dioxane	DMF	Pyridine
CS (BS)-F ^b		+	—	+	+	+	+
SA-F ^c		—	—	+	+	+	+
PHBA-F ^d		—	—	+	+	+	+
	CS (BS).SA.F	—	—	—	+	+	+
	CS (BS).PHBA.F	—	—	—	+	+	+
PAS-F ^e		—	—	—	—	—	+
PABA-F ^d		—	—	—	—	—	+
	CS (BS).PAS.F	—	—	—	—	+	+
	CS (BS).PABA.F	—	—	—	—	+	+
PC-F ^d		—	—	—	+	+	+
PCP-F ^f		—	—	+	+	+	+
	CS (BS).PC.F	—	—	—	—	+	+
	CS.PCP.F	—	+	+	+	+	+
	BS.PBP.F	—	+	+	+	+	+

Table 2. Characterization of copolymers.

Copolymer	Nitrogen	Halogen ^a	Copolymer composition from halogen content	Conductometric titration of copolymers (in pyridine against TBAH base)			$\bar{M}_n$ by VPO	$[\eta] \times 10^{20}$ dl. g ⁻¹ cr
				m mol of base added at first break of titration curve	m mol of base added at final break of titration curve	degree of polymerization $DP = Y/X$		
			CS or BS :: comonomer	X	Y			
CS.SA.F	..	6.2	0.175 : 0.450	90	630	7	1150	3.6
BS.SA.F	..	13.34	0.150 : 0.430	85	585	7	1250	3.8
CS.PHBA.F	..	5.7	0.160 : 0.470	80	645	8	1330	3.85
BS.PHBA.F	..	12.03	0.150 : 0.440	75	595	8	1430	4.1
CS.PAS.F	4.8	7.7	0.220 : 0.360	70	570	8	..	4.0
BS.PAS.F	4.4	17.85	0.225 : 0.285	65	520	8	..	4.2
CS.PABA.F	4.3	10.75	0.300 : 0.295	75	605	8	..	4.5
BS.PABA.F	3.9	20.02	0.25 : 0.280	70	550	8	..	4.65

^aan error nearly 2% of the reported value has been noted on an average.^bin 80 : 20 (v/v) DMF/water containing 1.0% KBr.

A mixture of CS (3.45 g, 0.02 mole), SA (2.76 g, 0.02 mole), 37% formaldehyde solution (3.45 ml, 0.04 mole) and 40 ml 5 M H_2SO_4 was refluxed with good stirring at 130° C for 6 hr. During this time, the solid product separated out. It was filtered and washed with hot water. The air-dried polymer sample was Soxhlet-extracted with benzene to remove unreacted monomers. The copolymer sample was dissolved in ethanol and reprecipitated as a pasty mass by adding distilled water. The pasty mass was washed by decantation and collected. It was dissolved in dilute alkali and reprecipitated by gradual addition of dilute HCl with stirring. The solid was allowed to settle and filtered by decantation. It was washed with water and allowed to dry in air.

The dried sample was powdered and stirred with acetone (30 ml) for about half an hour. The solid was filtered, washed and retreated in the same manner with acetone. This was repeated till the soluble portion was completely removed. The residue was copolymer. It was soluble in 1,4-dioxane, THF and DMF. It did not melt up to 360° C, yield 2.5 g.

2.1a. The copolymer samples labelled as BS.SA.F, CS.PHBA.F and BS.PHBA.F were prepared and treated in the manner described above.

2.1b. *Treatment of copolymers designated as CS.PAS.F, BS.PAS.F, CS.PABA.F and BS.PABA.F:* Each of the copolymer samples CS.PAS.F, BS.PAS.F, CS.PABA.F and BS.PABA.F prepared by the method described above was washed repeatedly with acetone. The residue was extracted with DMF leaving a small amount of insoluble material. The latter was rejected. The copolymer was precipitated from the DMF extract by diluting it with water. The solid, obtained on filtration and washing, was dried and treated again with acetone. The residue was the required copolymer. The yields are: CS.PAS.F, 3.5 g; BS.PAS.F, 3.2 g; CS.PABA.F, 3.0 g and BS.PABA.F, 3.0 g.

2.1c. *Treatment of copolymer samples designated as CS.PC.F and BS.PC.F:* The copolymer samples CS.PC.F and BS.PC.F were treated repeatedly with 2% aq. sodium hydrogen carbonate solution (50 ml) and then washed with 1,4-dioxane (20 ml). The residue was dissolved in DMF, filtered and diluted with water to precipitate the copolymer. The yields of copolymers are: CS.PC.F, 3.2 g, BS.PC.F, 3.0 g.

2.1d. *Treatment of copolymer samples designated as CS.PCP.F and BS.PBP.F:* Each of the copolymer samples CS.PCP.F and BS.PBP.F was treated with 2% aq. sodium hydrogen carbonate solution (50 ml) and then dissolved in solvent ether (30 ml) and filtered. The residue was the homopolymer of *p*-chloro or bromophenol. The solution of the copolymer in ether was evaporated to dryness. The solid was collected. It was soluble in ethanol, 1,4-dioxane, THF and DMF. The yields of copolymers are: CS.PCP.F, 3.0 g; BS.PBP.F, 2.5 g.

Halogen content in all copolymer samples was estimated by the Carius method. In the case of nitrogen containing copolymers, nitrogen content was estimated by Duma's method. The results are presented in table 2.

3.2. *IR spectra* of all copolymer samples were taken in KBr on Beckmann IR-5 spectrophotometer.

3.3. *Number average molecular weights (M_n)* of soluble copolymers were estimated by vapour pressure osmometry (VPO) in 1,4-dioxane at 51° C and also by non-aqueous conductometric titration.

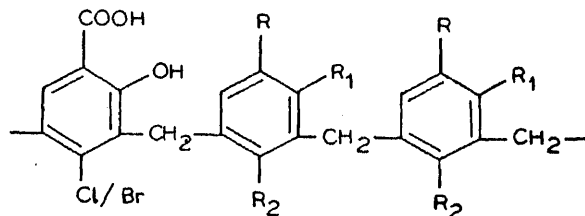
Conductometric titration of each of the copolymer samples was carried out in pyridine against standard tetra-*n*-butylammonium hydroxide (TBAH). In case of copolymers containing phenolic OH groups conductometric titration was also carried out in pyridine against standard sodium methoxide (NaOMe). The details of the procedure are reported in the literature (Chatterjee and Gupta 1971, 1974, 1977). The results are presented in tables 2 and 3.

3.4. *Viscometric measurements* of the solutions of the copolymer samples were carried out using Ubbelohde viscometer. Viscosity of all copolymer samples was measured in DMF and 80 : 20 (v/v) DMF/water containing 1.0% KBr. Intrinsic viscosities of all the copolymers are presented in tables 2 and 3.

3.5. *Thermogravimetry* of all the copolymer samples was carried out on "Du Pont-950 thermogravimetric analyzer" in CO₂ atmosphere at a heating rate of 10° C per min.

4. Results and discussion

The polymer samples, salicylic acid-formaldehyde (DeGeiso *et al* 1962), *p*-aminosalicylic acid-formaldehyde (Patel *et al* 1981), *p*-hydroxybenzoic acid-formaldehyde, *p*-aminobenzoic acid-formaldehyde and *p*-cresol-formaldehyde (Chatterjee 1970, 1971), polymers are all reported to have linear structures. As both the comonomers employed in the present copolymer synthesis are bifunctional, these copolymers would be linear. The distribution of the comonomer units along the polymer chains would be random. On the basis of this the following structure can be assigned to the copolymers.



I : R = COOH or CH₃ or Cl or Br⁻, R₁ = H and R₂ = OH or NH₂

II : R = COOH, R₁ = OH and R₂ = H or NH₂.

Table 3. Characterization of copolymers.

Copolymer sample	Conductometric titration of copolymers						Degree of polymerization	$\bar{M}_n$ by VPO	Copolymer composition	Halogen ^c content %	$[\eta] \times 10^2$ dl. g ⁻¹
	Total COOH + OH groups (titration against NaOMe base)	Total COOH groups (titration against TBAH base)	Total OH groups of phenolic comonomer added at first break of titration curve	OH groups of NaOMe base	m mol of TBAH or NaOMe	m mol of OH groups					
	m mol A	m mol B	m mol A - B = C	m mol A - 2B	D	D	DP = C/D				
CS.PC.F	890	206	684	476	98	7	..	0.205 : 0.475 ^a 0.205 : 0.510 ^b	7.3	3.4	
BS.PC.F	837	195	645	450	90	7	..	0.195 : 0.450 ^a 0.185 : 0.470 ^b	15.0	3.75	
CS.PCP.F	935	368	365	200	120	5	810	0.370 : 0.200 ^a	21.28 20.16 ^d	2.5	
BS.PBP.F	790	310	480	170	100	5	1030	0.310 : 0.170 ^a	36.66 38.40 ^d	2.4	

^aFrom conductometric titration, ^bfrom halogen content, ^can error 2% of reported value has been noted on an average, ^dcalculated from copolymer composition, ^ein 80 : 20 (v/v) DMF/water containing 1% KBr.

spectra of the copolymer samples.

Examination of the IR spectra shown in figures 1 and 2 reveal that they comprised a broad absorption band from 3500 to 2600 cm^{-1} due to OH and/or NH stretching vibrations. Such bands comprised distinct inflections at 3030, 2930, and 2850 cm^{-1} and are expected due to aromatic C-H and bridge-methylene C-H stretching. Separate carbonyl bands corresponding to two different C=O could not be observed in the spectra of copolymers obtained from comonomer acids. Only a slightly broad band covering expected vicinal positions is observed. In some spectra at least one inflection is observed in this broad band. Hence the average position of $\nu_{\text{C=O}}$ in the spectrum of each copolymer is noted in tables 2 and 3.

There is no clear indication of the presence of bands due to $-\text{CH}_2-\text{O}-\text{CH}_2-$ in the IR spectrum. Because of the relatively small proportion of this type of bridge and because of poorly resolved IR spectrum it is likely that the presence of the band due to $-\text{CH}_2-\text{O}-\text{CH}_2$ grouping may not have been observed. Hence no definite conclusion can be drawn about the presence or absence of such bridges in the polymer chains.

The average degree of polymerization ($\overline{DP}$) of copolymers estimated by non-aqueous conductometric titration is shown in tables 2 and 3. The values varied

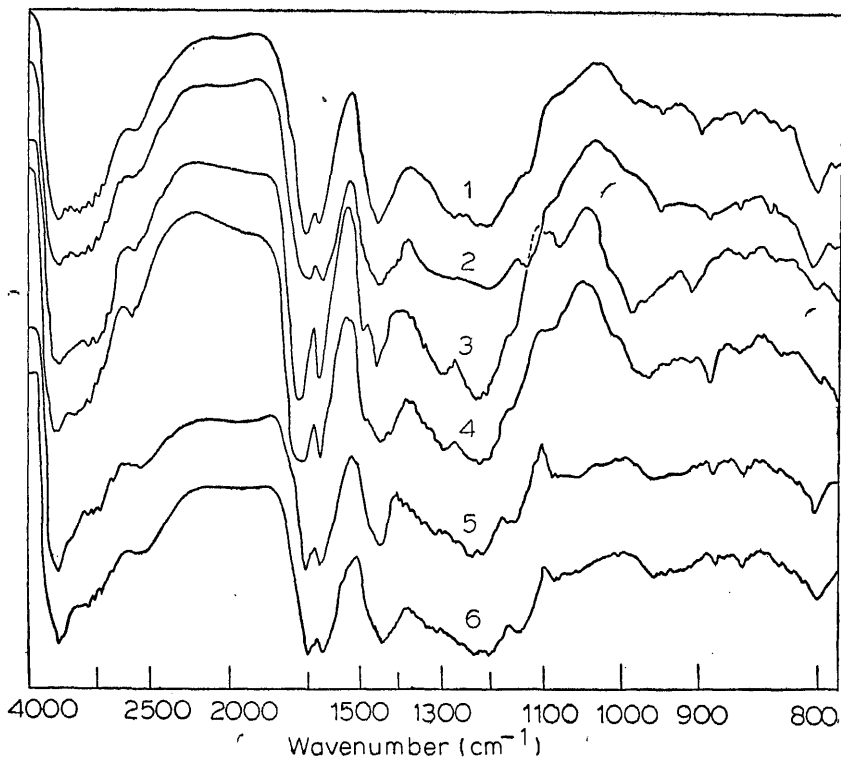


Figure 1. IR spectra of copolymer samples: 1. C3SA-E, 2. PS-SA-E,

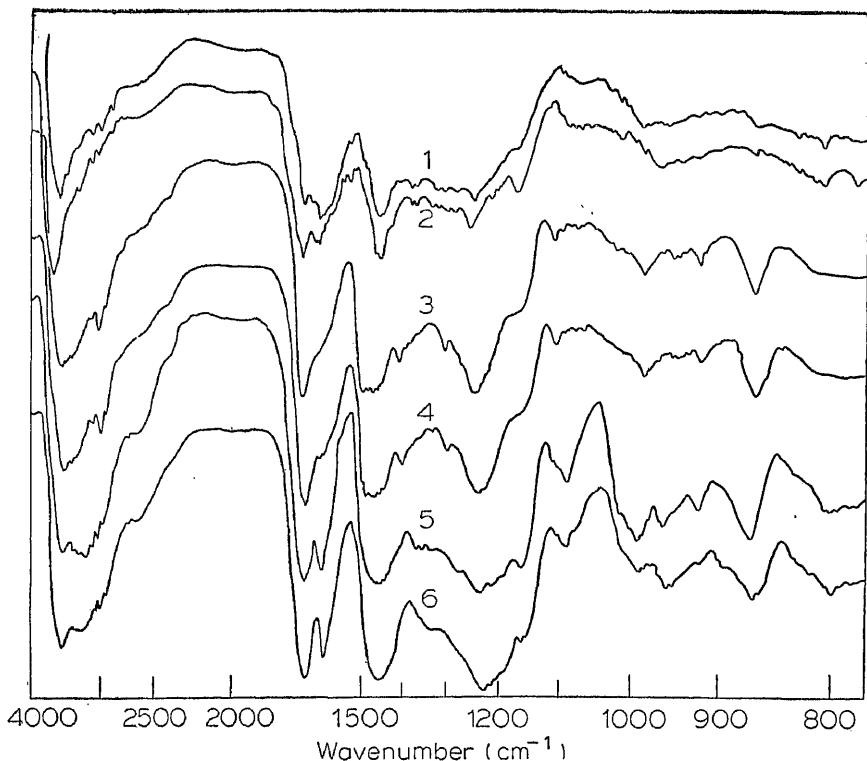


Figure 2. IR spectra of copolymer samples : 1. CS.PABA.F, 2. BS.PABA.F, 3. CS.PC.F, 4. BS.PC.F, 5. CS.PCP.F, 6. BS.PBP.F.

from 5 to 8 and are nearly consistent with the number average molecular weight ($\bar{M}_n$) of dioxane soluble copolymers estimated by VPO method. These lower values are expected as all the comonomers employed in the copolymerization reaction except *p*-cresol are much less reactive than phenol in phenol-formaldehyde reaction. The lowering of reactivity in the electrophilic substitution reaction is due to the presence of deactivating COOH and/or halogen.

On the basis of the percentage of Cl or Br in the copolymer sample it is possible to calculate copolymer composition of a copolymer if the other comonomer does not contain halogen. On the basis of percentage of Cl the total number of moles of 4-chlorosalicylic acid repeating unit (x) in 100 g of copolymer is given by

$$x = \text{percentage of Cl} \div 35.5.$$

Hence the wt. percentage of 4-chlorosalicylic acid repeating unit in the co-

∴ Copolymer composition will be given by the molar ratio

4-Chlorosalicylic acid repeating unit : Comonomer repeating unit
= $x : y$

In the case of copolymer obtained from nitrogen containing comonomer the composition based on halogen content of the copolymer can be used to calculate the expected N%. These values along with those of estimated N% are shown in table 2.

In the case of copolymers prepared from Cl or Br containing comonomers the data obtained from titration were employed to calculate copolymer composition. The titration against standard sodium methoxide in pyridine furnished information about total number of moles of both COOH and phenolic OH groups. The titration against standard TBAH would furnish information about only COOH groups (Chatterjee 1970). It can be shown that if the amount of 1 M TBAH required for 1 g of copolymer is equal to a ml and amount of 1 M NaOMe required for 1 g of copolymer is equal to b ml, the ratio $a : (b - 2a) = 4\text{-chloro-salicylic acid repeating unit} : \text{phenolic comonomer repeating unit}$.

The copolymer composition of copolymer containing *p*-cresol comonomer has also been estimated by a similar method. It was found that the copolymer composition estimated by this method compared well with the copolymer composition calculated on the basis of halogen content. The results are shown in table 3.

It is worth noting that the copolymer composition is highly dependent on the accuracy of the measured value of appropriate characteristic of one of the two comonomers. In the present cases there would be uncertainty in the measured property on the basis of which the copolymer composition is calculated. Hence information about the copolymer composition will not be that accurate as to permit a further detailed analysis. The predicted relative reactivity of 4-halo-(chloro, bromo) salicylic acid and the other comonomer in normal to homopolymerization is retained even in its copolymerization reaction. This order can be predicted on the basis of the structure of the comonomer. A phenol containing electron attracting groups shows lower reactivity in its reaction with formaldehyde. This is found to be true even in copolymerization reaction.

It was observed that all the copolymer samples showed polyelectrolyte behaviour in their solutions in DMF. This type of behaviour of a typical copolymer sample, CS.SA.F, was suppressed by increasing polarity of the solvent by using solvent/water mixture or by adding electrolyte to the solvent. By carrying out some experiments using various DMF/water mixtures as solvents and using different amounts of KBr, it was found that polyelectrolyte behaviour is suppressed in 80 : 20 (v/v) DMF/water containing 1.0% KBr by weight. Hence the viscometric study of all copolymer samples was carried out in 80 : 20 (v/v) DMF/water containing 1.0 % KBr by weight. From the plots of reduced viscosity vs. concentration the values of intrinsic viscosities of all copolymers were estimated. These values are shown in tables 2 and 3.

Table 4. Thermogravimetric analysis of copolymers.

Copolymer samples	Percentage weight-loss at temperature °C T							Temp. range for first step decom.	Weight-loss at first stage degradation %	
	100°	200°	300°	400°	500°	600°	700°		Calcd.	Observed
CS.SA.F	4	6	18	34	60	94		250-330	27.50	24
BS.SA.F	4	6	19	42	68	96		250-330	25.52	23
CS.PHBA.F	4	7	18	36	68	98		250-320	27.72	21
BS.PHBA.F	2	8	20	49	67	100		250-320	25.52	21
CS.PAS.F	6	9	26	36	74	100		250-300	25.52	26
BS.PAS.F	5	7	20	44	70	96		250-300	22.66	20
CS.PABA.F	7	10	28	48	78	94		250-300	26.20	28
BS.PABA.F	4	6	20	43	72	98		250-300	23.32	20
CS.PC.F	1	10	16	23	40	100		250-300	9.02	10
BS.PC.F	5	10	18	32	68	98		250-300	8.60	10
CS.PCP.F	1	4	17	21	31	42	52	250-300	16.20	17
BS.PBP.F	..	4	16	26	46	57	64	250-300	13.65	16

Examination of TG analysis results reported in table 4 reveals that each copolymer sample undergoes degradation in two steps. It is reported that salicylic acid-formaldehyde (SA-F) (DeGeiso *et al* 1962), *p*-aminosalicylic acid-formaldehyde (PAS-F) (Patel *et al* 1981) and *p*-chloro (or bromo) salicylic acid-formaldehyde (CS-F or BS-F) (Patel and Patel 1982) polymers undergo degradation in two steps. The first step in degradation of the above-mentioned SA-F type polymers and which appears from 200-300° C, depending upon the nature of the polymer, is attributed to the decarboxylation of the "salicylic acid units" present in the polymer chain. It has been observed that *p*-hydroxybenzoic acid-formaldehyde and *p*-aminobenzoic acid-formaldehyde polymers (Patel 1977) degrades in a single step when heated in air at a controlled rate.

The phenolic resins are reported to undergo one step random degradation when heated in air affording low molecular weight compounds (Jackson and Conley 1964). On the basis of these reported observations it is considered that the first step in the thermal degradation of the copolymers reported in table 4 may be due to decarboxylation and further degradation in the second step may be a random degradation reaction affording simpler degradation products.

On the basis of the copolymer composition of all the copolymers the possible % weight-loss due to decarboxylation in the first stage of degradation is calculated for all the copolymer samples. The values of the calculated % weight-loss are shown in table 4. The calculated values are found to be comparable with the observed values of % weight-loss at the end of the first step of degradation. This confirmed the view that the first step in degradation of the copolymers is due to

product and their relative proportion it is not possible to draw any further conclusion about the mechanism of degradation reaction of the copolymers.

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Dynamic distortion of C_4N^+ -skeleton in $(CH_3)_4NCl$

H D BIST*, MAHENDRA PAL, G S RAGHUVANSHI and
V N SARIN

Department of Physics, Indian Institute of Technology, Kanpur 208 016, India

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Abstract. The polarization data and concentration dependence of the Raman spectra of aqueous solutions of tetramethyl ammonium chloride in the region $2700\text{--}3100\text{ cm}^{-1}$ are studied. Group theoretically consistent assignments reveal that the C_4N^+ -skeleton acquires a dynamic distortion to C_{3v} symmetry due to out-of-phase combinations of the four CH_3 -stretching oscillations.

Keywords. Raman spectra; tetramethyl ammonium chloride; dynamic distortion.

Introduction

Tetramethyl ammonium ion $[(CH_3)_4N^+]$, henceforth abbreviated as TMA, retains high symmetry T_d over a wide range of environmental variations. Preliminary qualitative vibrational assignments, comprising of Raman (R) and infrared (IR) studies, are available in the literature (Edsall 1937; Ebsworth and Sheppard 1959; Bottger and Geddes 1965; Stanley and Tobin 1972; Harman *et al* 1974; Sonder Ohe 1975; Berg 1975; Kabisch and Klose 1978; Kabisch 1980). However, the assignments of internal vibrations of TMA are still at a controversial stage (Ebsworth and Sheppard 1959; Stanley and Tobin 1972; Berg 1975; Kabisch and Klose 1978), especially in the CH_3 -stretching region. Raman and IR studies of the polycrystalline compounds containing TMA have been reported recently (Kabisch 1980; Kabisch and Klose 1978). Kabisch *et al* (1978) studied the effect of varying concentration of tetramethyl ammonium chloride (TMAC) in D_2O , on the CH_3 -stretching modes; the abnormally high intensities of the bands assigned as combinations and overtones in the CH_3 -stretching region were attributed to the ion associations occurring in concentrated solutions.

In this paper we report the concentration dependence and polarization data of the Raman spectra of TMAC in aqueous solutions in the region $2700\text{--}3100\text{ cm}^{-1}$. The three strong polarized bands in this region are assigned as T_d -symmetric modes due to a dynamic distortion of C_4N^+ -skeleton, consistent with the group theoretical analysis.

2. Experimental

AR-grade TMAC obtained from Fluka was kept under vacuum at 300 K (RT) to remove any moisture from this very hygroscopic compound. The aqueous solutions of known concentrations were prepared from the moisture free compound. The Raman spectra were recorded on a Spex Ramalog spectrophotometer. The 514.5 nm beam obtained from a Spectra Physics 165-09 Ar⁺ laser was used to excite the Raman scattering. The scattered light was focussed into the entrance slit at the usual 90° geometry. The reported wavenumbers of the sharp and strong bands are correct to $\pm 1 \text{ cm}^{-1}$.

3. Group theoretical consideration

In tetramethyl ammonium compounds the symmetry of the whole TMA group will be T_d , if all the four methyl groups in it retain a staggered or an eclipsed configuration. Hence the distribution of vibrations for the TMA ion for both the staggered and the eclipsed configurations remains unchanged. The 45 degrees of vibrational freedom Γ_{vib} of TMA are distributed on the symmetry species of point group T_d as follows (Berg 1975) :

$$\Gamma_{\text{vib}} = 3A_1 + 1A_2 + 4E + 4F_1 + 7F_2.$$

Out of these, the A_1 , E and F_2 species are Raman active and only the F_2 species are IR active.

A correlation of isolated CH_3 -stretching vibrations (C_{3v} point group) with those of TMA under T_d and C_{3v} point groups is given in table 1. Under the group T_d in TMA the C-H symmetric stretching (A_1) vibrations of four isolated CH_3 groups produce a totally symmetric species A_1 and a triply degenerate species F_2 . Likewise, the four isolated CH_3 -asymmetric stretching modes (E) under C_{3v} produce a doubly degenerate E species and two triply degenerate species F_1 and F_2 under T_d point group as shown in the second column of table 1. As a result under the point group T_d one expects, in the CH_3 stretching region, four Raman active bands out of which only one should exhibit totally symmetric and polarized (A_1) character.

If the C_4N^+ group of TMA acquires a C_{3v} symmetry even dynamically (e.g., this could be the case during its ν_3 vibration as discussed later and shown in figure 1) the situation gets changed as illustrated in the third column of table 1. It is evident that one would expect a maximum of three totally symmetric polarized (A_1) CH_3 -stretching bands along with four doubly degenerate (E) depolarized C-H stretching modes. This situation will be applicable to the solutions where the crystalline field effects would be missing.

4. Results and discussion

Table 1. Correlation of the CH_3 -stretching vibrations having point group C_{3v} with corresponding vibrations in TMA having symmetries T_d or C_{3v} .

CH ₃ -stretching vibrations		
Isolated CH ₃	CH ₃ in TMA units	
C_{3v}	T_d	C_{3v}
Totally symmetric CH ₃ -stretching vibration, $A_1(R)$	$A_1(R)$ $F_2(R, IR)$	$A_1(R(p), IR)$ $A_1(R(p), IR)$ $E(R(dp), IR)$
Asymmetric CH ₃ -stretching vibration, $E(R, IR)$	$E(R)$ F_1 $F_2(R, IR)$	$E(R(dp), IR)$ $E(R(dp), IR)$ A_2 $E(R(dp), IR)$ $A_1(R(p), IR)$

The notations regarding species are discussed in the text. The activities in Raman (R) and Infrared (IR) are given for ready reference. *p*—polarized, *dp*—depolarized.

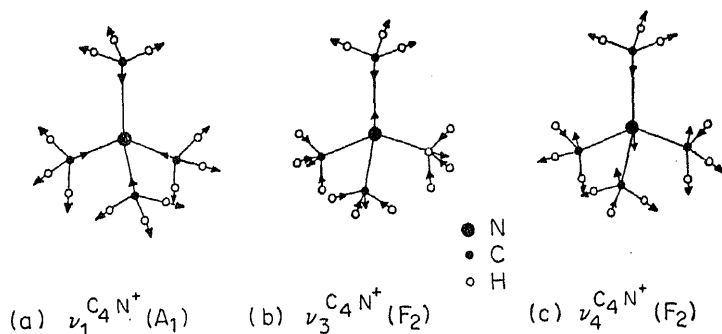


Figure 1. Diagrammatic representation of the three totally symmetric CH-stretching motions of CH_3 in tetramethyl ammonium ion. (a) The T_d symmetry is retained, (b) and (c) the symmetry will be dynamically distorted to C_{3v} (cf. column III in table 1).

are shown in figure 2. In figure 3 the normal Raman spectra for 0.4 M and 0.0 M aqueous solutions in the same region are presented. Table 2 summarises the wavenumbers (cm^{-1}), relative peak intensities, half-widths, relative integrated intensities and polarization characteristics of the bands observed in the regions 400 to 1500 cm^{-1} and 2700 to 3100 cm^{-1} . The assignments of the bands observed in these regions, based on two alternative considerations (i.e., Fermi-resonance and anharmonicity and dynamic distortion of C_4N^+ -skeleton) are proposed in the

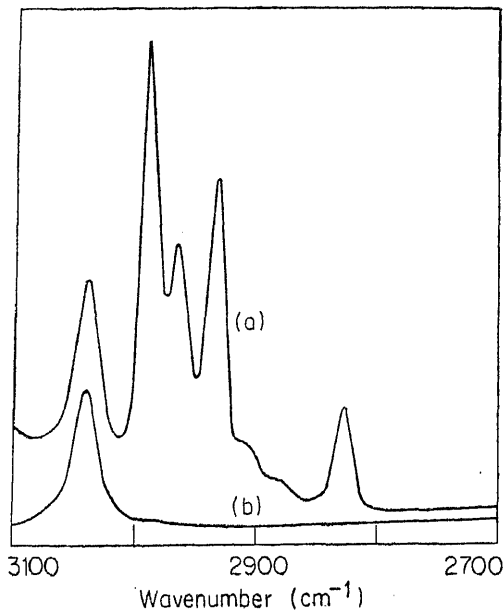


Figure 2. Raman spectra (514.5 nm exciting laser beam with power on the sample ~ 150 mw) of tetramethyl ammonium chloride in aqueous solution of ~ 0.4 M in quartz cell at right-angle geometry. (a) Parallel and (b) perpendicular polarizations.

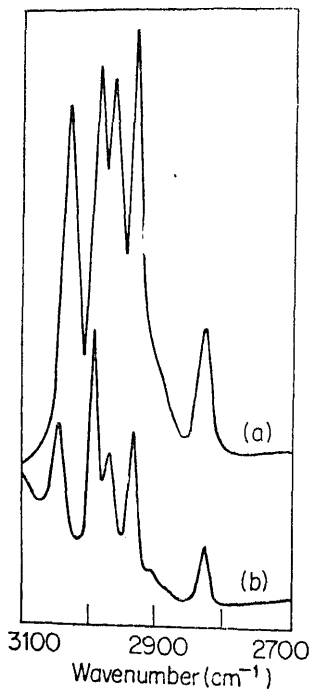


Figure 3. Raman spectra of tetramethyl ammonium chloride in aqueous solution of ~ 0.4 M in quartz cell at right-angle geometry. (a) Parallel and (b) perpendicular polarizations.

Table 2. Wavenumbers (cm^{-1}) of the observed bands and their assignments in the aqueous solutions of tetramethyl ammonium chloride in the regions 1400–1500 cm^{-1} and 2700–3100 cm^{-1} .

Dilute solution (0.4 M)		Concentrated solution (7.0 M)		Assignments	
1	2	3	4	5	6
26 (<i>dp</i>) 5, 20, 6)	..	1422 (<i>dp</i>) (1.2, 20, 7)	..	$\nu_{18}(F_2)$	$\nu_{18}(F_2)$
56 (<i>dp</i>) 8, 18, 33)	..	1456 (<i>dp</i>)	..	$\nu_8(E)$	$\nu_8(E)$
85†		1485†		$\nu_{15}(F_2)$	$\nu_{15}(F_2)$
26 (<i>p</i>) 6, 16, 21)	2852 (26)	2824 (<i>p</i>) (4.6, 21, 30)	2844 (20)	$2\nu_{10}(F_2)$	$2\nu_{10}(F_2)$
78*)	2882 (4)	2878* (—)	2878 (0)	$\nu_{10}(F_2) + \nu_8(E)$	$\nu_{10}(F_2) + \nu_8(E)$
106*)	2912 (6)	2906* (—)	2912 (6)	$2\nu_8(E)$	$2\nu_8(E)$
30 (<i>p</i>) 0, 15, 60)	2941 (11)	2928 (<i>p</i>) (15, 24, 114)	2941 (13)	$\nu_8(E) + \nu_{15}(F_2)?$	$\nu_8(A_1)$
56 (<i>p</i>) 2, 18, 63)	2970 (4)	2961 (<i>p</i>) (13.4, 18, 76)	2970 (4)	$2\nu_{15}(F_2)$	$\nu_8(A_1)$
39 (<i>p</i>) 8, 18, 119)	..	2986 (<i>p</i>) (14, 23, 102)	..	$\nu_1(A_1)$	$\nu_8(A_1)$
43 (<i>dp</i>) 3, 28, 100)	..	3031 (<i>dp</i>) (12.6, 25, 100)	..	$\nu_5(E)$ $\nu_{13}(F_2)$	$\nu_8(E)$

Columns 1 and 3 indicate the observed wavenumbers (cm^{-1}). The figures in parentheses under each wavenumber denote the relative peak intensity (arb. units), the half-widths (cm^{-1}) and relative integrated intensity respectively.

Columns 2 and 4 indicate the calculated harmonic values (cm^{-1}) of overtone/combination bands shown in column 5. The figures in parentheses in these columns represent the differences between the harmonic values (as expected from the assignments in column 5) and the actual observed wavenumbers shown in columns 1 and 3.

Columns 5 and 6 represent the assignments based on "Fermi-resonance and anharmonicity" and "dynamical distortion of the C_4N^+ -skeleton", respectively. The assignments in column 5 are reported by Kabisch *et al* (1978). Here we have used standard notations (see Berg 1975) in numbering the frequencies as $\nu_{18}(F_2)$, etc. The $\nu_8(A_1)$ in column 6 is the same as $\nu_1(A_1)$ in column 5.

and *dp* denote the polarized and depolarized character of bands.

Bands are observed in the infrared spectra.

Selection rules for overtones and combinations are

$$\times F_2 = A_1 + E + F_1 + F_2 \quad E \times E = A_1 + A_2 + E \quad E \times F_2 = F_1 + F_2.$$

drastically.

5. Fermi-resonance and anharmonicity

Our assignments, shown in column 5 of table 2 are analogous to those proposed by Kabisch *et al* (1978). The moderate intense band at 2826 cm^{-1} (in 0.4 M solution) shows the largest mechanical anharmonicity and its intensity is about an order of magnitude smaller than that of the other strong polarized band. This band has been attributed to an overtone of the $\nu_{16}(F_2)$ mode. Similarly the other very weak bands at 2878 and 2906 cm^{-1} (in 0.4 M solution), with less anharmonicities, are assigned to a combination and an overtone band respectively.

The assignments of the bands in the region 1400 to 1500 cm^{-1} are based on several unambiguous arguments including the Teller-Redlich product rule (Berg 1975 ; Herzberg 1960). The depolarized band at 3043 cm^{-1} and the polarized band at 2989 cm^{-1} can safely be assigned to the CH_3 -asymmetric and the CH_3 -symmetric stretching modes respectively. The polarized band at 2966 cm^{-1} can also be justified as the allowed A_1 component of the overtone of $\nu_{15}(F_2)$ mode. The other polarized band at 2930 cm^{-1} cannot be assigned as the combination of the $\nu_6(E)$ and the $\nu_{15}(F_2)$ modes.

In general, due to Fermi-resonance, the resonating band which is nearer to the fundamental gains more intensity than the band farther from it. Neither the Fermi-resonance nor the electrical anharmonicity consideration can explain the observed intensity distribution and its variation with concentration. The Fermi-resonance combined with the electrical anharmonicity (coupled with mechanical anharmonicity) may explain the observed abnormal intensity distribution. One may argue that the band at 2930 cm^{-1} may have more electrical anharmonicity (as would be expected on the basis of higher mechanical anharmonicity) than the band at 2966 cm^{-1} , making it (2930 cm^{-1} band) more intense after Fermi-resonance than the band at 2966 cm^{-1} which is closer to the fundamental at 2989 cm^{-1} . However, this argument is untenable due to the following reasons :

- (i) The fundamental requirement for the Fermi-resonance is that the levels involved must have the same symmetry (Herzberg 1960). The selection rules show that the combination of $\nu_6(E)$ and $\nu_{15}(F_2)$ produces levels of symmetry species F_1 and F_2 , out of which species F_2 cannot resonate with CH_3 -symmetric mode which is of symmetry species A_1 .
- (ii) The intensity of the resonating band(s) can never exceed the intensity of the fundamental band, unless electrical anharmonicity is a dominating factor which is seldom observed in Raman spectra.
- (iii) It is observed that on varying concentration, the intensities of the resonating bands change drastically whereas the band positions remain almost unchanged. This is also not observed in Fermi-resonance especially when the positions of fundamental bands remain unchanged.

Thus the intense and the polarized band at 2930 cm^{-1} cannot unambiguously

an alternative explanation of the three strong polarized and intense bands may be searched in the dynamic distortion of C_4N^+ skeleton.

6. Dynamic distortion of C_4N^+ -skeleton

The totally symmetric CH_3 stretching motions of the four CH_3 groups in TMA ion could result in three specific configurations consistent with the internal vibrations of C_4N^+ -group as shown in figure 1. In the first configuration (figure 1a) all the C-atoms vibrate in phase along C-N bonds. In this case the T_d symmetry of the C_4N^+ -skeleton is maintained even dynamically. This situation corresponds to ν_1 mode of species A_1 for the skeleton and yields one totally symmetric polarized CH_3 -stretching vibration.

In the second configuration, three C-atoms vibrate in-phase and one out-of-phase and *vice versa* along C-N bonds as shown in figure 1(b). In this case the T_d symmetry of C_4N^+ -skeleton is distorted to C_{3v} dynamically corresponding to $\nu_3(F_2)$ mode for the skeleton (T_d) and yields under C_{3v} one A_1 totally symmetric polarized CH_3 -stretching mode and another asymmetric depolarized CH_3 -stretching mode (E).

In the third configuration, three C-atoms vibrate in-phase perpendicular to C-N bonds and one along the C-N bond as shown in figure 1(c). In this case, too, the T_d symmetry of C_4N^+ -skeleton is distorted to C_{3v} dynamically and the situation, corresponding to $\nu_4(F_2)$ mode for the skeleton (T_d), yielding one totally symmetric polarized CH_3 stretching mode (A_1) and another asymmetric depolarized CH_3 stretching mode (E).

There are two more possible configurations which produce two asymmetric depolarized CH_3 stretching modes corresponding to the vibrations of the C_4N^+ -skeleton of species E and F_1 . It can, therefore, be concluded that there must be three totally symmetric polarized C-H stretches due to dynamic distortion of C_4N^+ -skeleton and coupling between the four CH_3 groups. Thus the evidence for the three expected A_1 modes in CH_3 stretching region is unambiguously established.

The four CH_3 asymmetric stretches may appear at the same frequency giving thereby a single depolarized band at 3043 cm^{-1} (in 0.4 M solution). The larger half-width of this band and shift with concentration may also corroborate the presence of more than one unresolved bands under the combined envelope.

Acknowledgements

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ab initio molecular orbital study of thymine radicals[†]

U CHANDRA SINGH and A MURALIKRISHNA RAO*

Solid State and Structural Chemistry Unit, Indian Institute of Science,
Bangalore 560 012, India

MS received 18 March 1982

Abstract. *Ab initio* calculations at the STO-3G level have been carried out on the six thymine radicals, 1-yl, 6-yl, 5-yl, 7-yl, 4-hydroxyl and the anion. The results have been compared with those from ESR studies.

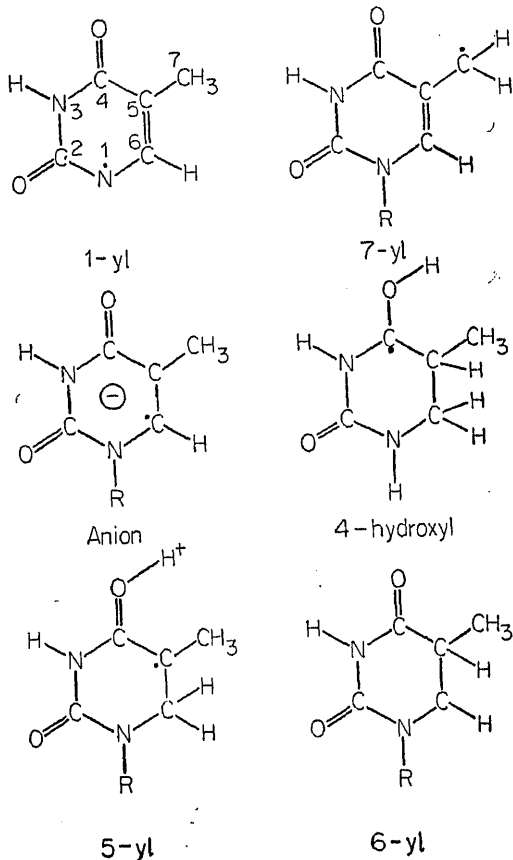
Keywords. Thymine radicals; molecular orbital calculations; radiation biology.

Introduction

One of the most well-known radicals in radiation biology is the thymine radical (Flossmann *et al* 1980), which is known to occur in different types (chart 1). Thymine is used as a model compound for analysing radicals generated by radiation through ESR spectroscopy. One of the first radicals of thymine to be examined was the 5-yl radical (Pruden *et al* 1965) and since then a number of papers have appeared on the different radicals of thymine. Various radicals produced in single crystals of thymine derivatives by UV and x-radiations have been investigated recently through ESR spectroscopy by Flossmann *et al* (1980). The first attempt to study the radicals theoretically was made by Heiberg and Jensen (1977) who employed the semi-empirical INDO method, and found that the INDO method does not yield satisfactory agreement with ESR studies. We considered it desirable to perform *ab initio* calculations on various thymine radicals in view of their obvious importance to radiation biology.

Method of calculation

Calculations were performed at the minimal STO-3G level (Hehre *et al* 1969). For each radical species, one basic set of structural parameters was developed. While some of the optimized INDO parameters (Heiberg and Jensen 1977) were chosen for the purpose, most bond angles and some of the bond lengths were chosen with some guidance from the results of the crystallographic investigation



of thymine derivatives (Gerdil 1961). In the case of the 1-yl radical, bond distances, such as N1-C6, N1-C2 and C4-O8, were optimized.

Since the UHF calculations mix up the higher spin-component wavefunctions, spin densities calculated by the UHF method cannot be correlated with experiment well. Hence, all the spin densities were calculated after annihilating the unwanted higher spin multiplets using the spin-annihilation procedure (Amos and Snyder 1961; Snyder and Amos 1965). In general, two annihilations were needed to get rid of the contribution of the higher spin-states. ENDOR experiments on the methyl protons in thymine radical in irradiated thymidine is known to show a large potential barrier to rotation. Hence, the spin properties of the methyl protons were calculated only for a single conformation and averaging over the angles was not performed.

3. Results and discussion

Expectation values of the spin operator $\langle S^2 \rangle$ given in table 1 shows that the $\langle S^2 \rangle$

of the spin densities before and after annihilation shows that the annihilation procedure reduces spin densities strongly.

In table 2, we have listed the calculated π and total spin densities at C, N and O atoms for all the radicals studied and in table 3, we list the calculated atomic spin densities at the hydrogen atoms. The calculated and experimental coupling constants for the radicals are given in table 4 while in table 5 we have listed the Mulliken populations.

Table 1. The $\langle S^2 \rangle$ values and the relative energies of the radicals.^a

Radical	$\langle S^2 \rangle_{aa}$	$\langle S^2 \rangle_{sd}$	Relative energy kcal/mol
1-yl	0.7478	1.1706	0.0
6-yl	0.7495	0.7859	98.5
5-yl	0.7425	1.0503	114.4
7-yl	0.7654	1.3819	-3.8
anion	0.7529	0.9036	-47.9
4-hydroxyl	0.7578	1.3304	108.4

^a After annihilation (aa); singe determinant (sd).

Table 2. Calculated π and total spin densities at carbon, oxygen and nitrogen atoms.

Radical		C ₄	C ₅	C ₆	C ₇	N ₁	N ₃	O ₉	O ₈
1-yl	π	-0.058	0.403	-0.114	-0.004	0.421	-0.016	0.158	0.215
	Tot.	-0.082	0.451	-0.157	-0.023	0.449	0.015	0.163	0.222
6-yl		0.017	-0.019	0.861	0.014	0.062	-0.003	0.118	-0.002
		0.026	-0.094	1.017	0.033	0.035	-0.001	0.126	-0.026
5-yl		-0.102	0.659	-0.007	-0.007	0.002	-0.009	-0.015	0.396
		-0.149	0.728	-0.034	-0.035	0.004	-0.007	-0.016	0.414
7-yl		0.127	-0.119	0.434	0.531	0.037	0.013	0.079	-0.111
		0.166	-0.195	0.466	0.606	0.028	0.012	0.086	-0.125
anion		0.060	0.020	0.593	0.002	0.032	0.014	0.004	0.270
		0.054	-0.009	0.656	0.007	0.019	0.015	0.004	0.280
4-hydroxyl		0.385	-0.099	0.447	0.004	0.082	0.075	-0.119	0.039
		0.428	-0.157	0.501	0.010	0.074	0.067	-0.142	0.020

Radical	H(C5)	H(C6)	H(N1)	H(N3)	H(Me)	H(O8)
1-yl	..	0.006	0.00	0.0	0.019	..
6-yl	0.023	-0.060	-0.004	0.0	-0.002	..
5-yl	..	0.017	-0.0	0.0	0.018	..
7-yl	..	-0.018	-0.001	0.0	-0.022	..
anion	..	-0.023	-0.001	0.0	0.0	..
4-hydroxyl	..	-0.019	-0.005	-0.004	-0.004	-0.002

Table 4. Calculated and experimental coupling constants.

Radical	α -proton	β -proton (CH ₃)	β -proton (methylene)
1-yl	Exp	..	18.7
	<i>ab initio</i>	4.91	15.55
	INDO (sd)	6.60	19.35
6-yl		-48.0	17.4
		-49.1	18.81
		-38.1	17.6
	INDO (aa)	-32.8	7.9
5-yl		21.7	40.0
	..	14.72	13.91
		22.3	31.60
		19.2	26.5
7-yl		-9.7	..
		-14.72	..
		-12.10	..
		-5.3	..
anion		-14.3	
		-18.81	..
		-13.7	
		-6.0	
4-hydroxyl		-21.1	
		-15.54	..
		-12.70	
		-5.5	

Table 5. Mulliken population analysis for π -electrons.

Bond	1-yl	6-yl	5-yl	7-yl	anion	4-hydroxyl
N1-C6	0.092	0.015	0.002	0.021	-0.005	0.012
C6-C5	0.098	0.006	0.005	0.094	0.067	0.097
C5-C4	0.053	0.005	0.069	0.028	0.097	0.102
C4-N3	0.026	0.036	0.025	0.031	0.005	0.013
N3-C2	0.028	0.034	0.035	0.034	0.049	0.032
C2-N1	0.040	0.001	0.053	0.042	0.052	0.033
C2-O7	0.139	0.139	0.118	0.138	0.126	0.124
C4-O8	0.135	0.157	0.136	0.136	0.096	0.013
C5-C9	0.005	0.056	0.005	0.089	0.007	0.004

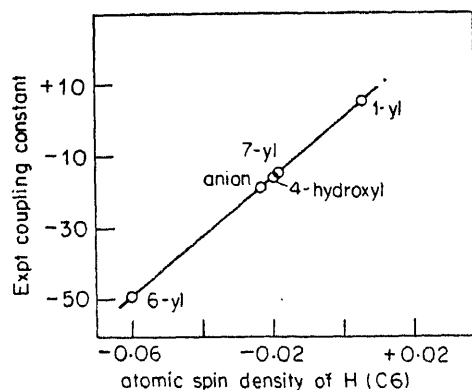


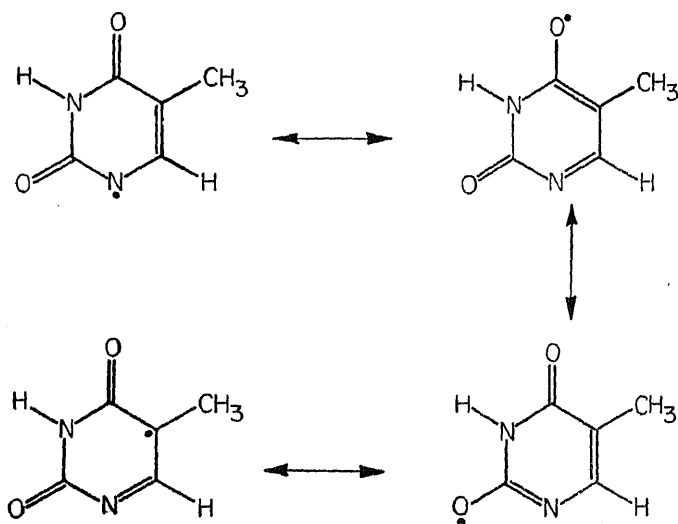
Figure 1. Plot of experimental coupling constant against atomic spin density of H (C6).

Since the hyperfine splitting constants are proportional to spin densities at a particular hydrogen atom, the calculated hydrogen spin densities were plotted against the experimental splitting constants. We see from figure 1 that there is a linear relation with a slope of 818.5 Gauss per unit spin density.

The UHF calculations make it possible to correlate the unpaired spin densities in the $2p_z$ atomic orbitals with the unpaired spin densities in the $2s$ -orbital of the carbon atoms. There is a linear relationship which justifies the use of McConnell's (1956) procedure to compare spin densities obtained by the RHF calculations with experimental values obtained from ESR spectroscopy. We shall now briefly

3.1 1-yl radical

The 1-yl radical resulting from the removal of the hydrogen in the N1 position has been observed in single crystals of anhydrous thymine (Dulic and Herak 1972). The radical is stable upto 300 K. The optimized values for the N1-C6, C5-C6 and C4-O8 distances in this radical are 1.389 Å, 1.375 Å and 1.264 Å respectively. Unpaired electron densities at the p_z orbitals of N1, C5 and O8 atoms are 0.421, 0.403 and 0.215 respectively; the unpaired electron is therefore localized on these sites. As examination of Mulliken's π -population analysis shows that there is considerable delocalization of the π -electrons in the ring. It is interesting that the lone pair electron at the N1 atom is in the plane of the ring just as in the case of pyridine molecule. The π -orbital charges at N1 is 1.024e while in all other radicals it is around 1.73e. Thus, the 1-yl radical could be depicted as follows:



This type of behaviour was also observed in uracil derivatives (Horan and Snipes 1970; Farley and Bernhard 1975; Zehner *et al* 1976). The ESR spectrum of 1-yl uracil radical shows the unpaired electron to be localized on the N1-atom (≈ 0.40). The calculated coupling constant for the methyl proton is 15.6 G which agrees with the experimental value of 18.05 G. Our INDO calculations predict a value of 19.35 G.

3.2 6-yl radical

The 6-yl radical was first analysed in detail by Henriksen and Snipes (1970) in a single crystal of dihydrothymine exposed to x-rays. Flossmann *et al* (1979) have also identified this radical in thymine irradiated at 230 K and in methyl thymine irradiated at 77 K. The 6-yl radical could be transformed into the

had found a value of 28.3 G for the α -proton coupling constant while Flossmann *et al* have found the value to be 48.0 G. Our calculations predict a value of 49.1 G which agrees well with that of Flossmann *et al*. Further, the experimental value of the β -proton coupling constant is 17.4 G which also agrees with the calculated value of 18.8 G. The Mulliken population analysis also shows that the π -electrons are localized on the carbonyl and there is little delocalization in the ring.

3.3 5-yl radical

The 5-yl radical was observed in both thymine and dihydrothymine and its derivatives. In dihydrothymine exposed to x-rays at 300 K, it is found to be present only as a minor fraction whereas it is predominant under similar conditions in the parent compound. According to our calculations, this is the most stable of all the thymine radicals. The spin densities at the C5 and O8 atoms are 0.659 e and 0.396 e respectively. Thus, the spin density is distributed between these two atoms. The calculated splitting constant for the methyl proton is 14.8 G which agrees well with the experimentally observed value. Our INDO calculations predict a value of 22.3 G. However, the methylene proton values are substantially lower than those obtained experimentally. The calculated value is 14 G, the experimental one being 40 G. According to our INDO calculations, the variation of the methylene group through rotation around the C5-C6 axis cannot increase the coupling constant substantially. In order to study the effect of the HCH angle on the coupling constant, calculations were carried out for two different angles. It was found that the decrease of the HCH angle to 72° only increased the coupling constant to 19.2 G. However, this increases the energy substantially (by about 210 kJ mol⁻¹). On the other hand, increase in the HCH angle to 137° decreased the coupling constant to 10.8 G while the energy increased by about 77 kJ mol⁻¹. One possible explanation would be the protonation of the carbonyl oxygen as suggested in the case of uracil derivatives (Zehner *et al* 1976 ; Flossman *et al* 1979). We could not carry out calculations due to convergence problem for the protonated species.

3.4 7-yl radical

This radical, originally proposed by Hüttermann (1970), was detected in several thymine derivatives except dihydrothymine. The radical is thermally stable upto 485 K. Our calculations show this radical to be as stable as the 1-yl radical. The calculated splitting constant for the C7 proton is 18 G which agrees well with the experimental value of 15.3 G. However, the calculated value for the C6 proton is 14.7 G which is somewhat higher than the experimentally observed one. The unpaired electron density seems to be located mostly on the C9 (0.606) and C6 (0.466) carbon atoms. The spin densities on the C5, C6 and C9 atoms as calculated by the INDO method are in agreement with the *ab initio* calculations.

3.5 Anion radical

Hydrated thymine irradiated with x-rays at 77 K exhibits a doublet ESR spectrum attributed to the anion radical. This radical is highly sensitive to light and heat

which are the characteristic of ionic radicals. This anion radical has also been observed in thymidine at 4.2 K. Our calculations show that the spin densities are localized on the C6 (0.656) and O8 (0.280) atoms resulting in the doublet splitting due to the α -proton. The calculated splitting constant for the C6 proton is 18.8 G which is close to the experimental value of 14.3 G. The calculations show that this radical is the least stable of all the thymine radicals.

3.6 4-hydroxy radical

In order to explain the doublet spectrum obtained at low temperatures, Henriksen and Snipes (1970) proposed the 4-hydroxy radical. However, later work showed the doublet to be due to the anion radical. We have carried out calculations on the 4-hydroxy radical which can be considered to be the protonated anion. Our calculations predict a high stability for this radical compared to other radicals. The unpaired electron density in this radical resides mainly on the C4 (0.429) and C6 (0.501) atoms. In the anion radical, the spin density on the C4 atom is very low (0.060) in contrast to this radical. Also, there is a large negative spin density on the O7 atom (-0.143) in contrast to the anion radical (0.004). However, the spin density distribution on the H-atom is remarkably similar. A comparison of the Mulliken population of π -electrons shows that, except in the C4-O7 bond, the populations are quite similar.

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EXAFS studies of cobalt oxides and oxide glasses†

R PARTHASARATHY, RAVI V PRASAD⁺, P R SARODE and
K J RAO*

Solid State and Structural Chemistry Unit, Indian Institute of Science,
Bangalore 560 012, India

MS received 31 December 1981

Abstract. The EXAFS of Co^{2+} has been studied in rare earth cobaltites and in sulphate and borate glasses. It has been found that the environment of Co^{2+} ions is very similar in these cases. It appears feasible to study local structures in glasses using probe ion EXAFS.

Keywords. EXAFS; ionic glasses; crystals.

1. Introduction

Rare earth cobaltites have been well investigated in recent years and their structures are known in sufficient detail (Raccah and Goodenough 1967; Demazeau *et al* 1974). An EXAFS study of such model compounds would be expected to furnish information (*e.g.*, phase-shifts) which could then be used in EXAFS analysis of glasses containing cobalt. Considering the comparative paucity of EXAFS data on crystalline compounds whose structure is known in detail, we felt that an EXAFS study of these compounds could also provide much insight on the scope of the technique itself.

In this paper we report results of EXAFS investigations of crystalline LnCoO_3 (where $\text{Ln} = \text{La}, \text{Nd}, \text{Dy}$ and Yb) compounds and of some cobalt-containing glasses belonging to the systems $\text{Na}_2\text{SO}_4\text{--K}_2\text{SO}_4\text{--ZnSO}_4\text{--CoSO}_4$ and $\text{CoO--B}_2\text{O}_3$. The ternary sulphate system $\text{Na}_2\text{SO}_4\text{--K}_2\text{SO}_4\text{--ZnSO}_4$ has been extensively studied in this laboratory (Sundar and Rao 1980; Sundar and Rao 1981). At low concentrations, the isovalent Co^{2+} ions are known to enter Zn^{2+} sites due to similarity of sizes (Sundar and Rao 1981). At higher concentrations, however, the site symmetry of the Co^{2+} ion is not known. A Co K-edge EXAFS study might be expected to yield valuable information on both concentration regimes.

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⁺ NSTS Scholar from I.I.T., Kanpur.

* To whom all correspondence should be addressed.

2. Experimental

The preparation of the rare earth cobaltites from the cobaltcyanide (Demazeau *et al* 1974) and of sulphate glasses from component sulphates (Sundar and Rao 1980) have both been reported earlier. Glasses with higher cobalt content were progressively more unstable with respect to devitrification. The Co-borate glass was prepared by melting together CoSO_4 and H_3BO_3 in a graphite crucible.

Co K-absorption edge EXAFS was measured using a bent crystal spectrograph and a Carl-Zeiss microdensitometer as described previously (Parthasarathy *et al* 1981). Data were available upto about 400 eV beyond the edge. Details with regard to the procedure for data analysis and Fourier transformation along with subsequent curve-fitting procedures have been described elsewhere (Cramer 1978 ; Parthasarathy *et al* 1982).

3. Results and discussion

Figure 1 shows the radial structure functions (RSF's) obtained for the crystalline compounds. Figure 2 shows the RSF's obtained for the glasses. Distances corrected for phase-shifts are listed in table 1.

3.1. Cobalt in rare earth cobaltites LnCoO_3

Rare earth cobaltites are known to crystallise in the perovskite structure (Demazeau *et al* 1974). The first peak in the RSF at $1.92 \pm 0.03 \text{ \AA}$ may be identified as the

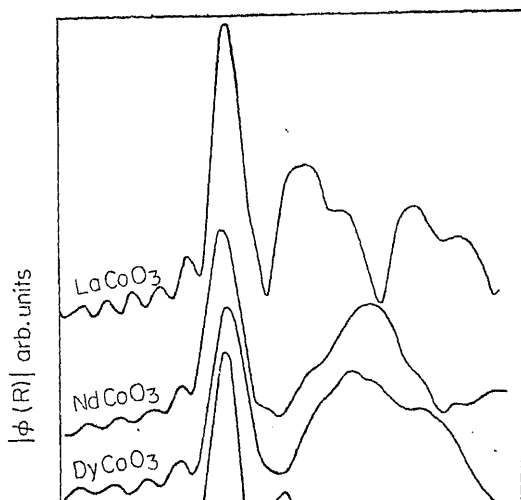


Table 1. Phase shifts and distances from RSF's of cobalt oxides and oxide glasses.

No.	Compounds	α^* (Å)	Distances (Å)						
1.	LaCoO ₃	0.034	1.91	2.05	2.91	3.35	4.25	4.71	
2.	NdCoO ₃	0.046	1.92		2.85	3.29	3.83	4.37	
3.	DyCoO ₃	0.020	1.96		2.83	3.26	3.80	4.34	
4.	YbCoO ₃	0.04	1.91	2.38	2.67	2.95	3.35	3.60	
5.	Sulphate Glass 1	0.081	2.02			3.42	4.61	5.73	
6.	Sulphate Glass 2	0.029	1.98			3.71	4.53	5.43	
7.	Sulphate Glass 3	0.073	2.02			3.31	3.85	4.57	
8.	Borate Glass	0.065	1.90			3.49	4.64	5.76	

Co-O distance. This distance is almost independent of the rare earth ion. Phase corrections were made using YbCoO₃ as a standard (Cramer 1978). For peaks other than the first, we felt that use of the curve fitting procedure was inadvisable since their amplitudes in the RSF were low. Phase corrections, α^* , were calculated using the expression,

$$\alpha^* = R_{\text{standard}} - R_{\text{fourier transform.}}$$

$|\alpha^*|$ was then added to the appropriate peak in the RSF's of the other cobaltites. The feature at 2.9 Å, however, is rather perplexing and we are unable to ascertain its origin from available crystal data.

3.2. Cobalt in glasses

3.2a Sulphate glasses : The similarity of the RSF's of these glasses to those of the crystalline cobaltites suggests that the co-ordination of Co²⁺ in these are similar. This is quite in keeping with the structural model proposed earlier for these glasses (Sundar and Rao 1980). On the basis of this model, we assign the peak at 1.90 Å to the Co-O distance. Similarly, the 3.7 Å peak may be assigned to the Co-K separation; the peak at 5.5 Å could possibly describe the Co-Co or Co-Zn distances.

At low Co²⁺ concentration, the sites that Co²⁺ ions may occupy are limited to those of Zn²⁺ ions in the glass. With these concentrations, one would expect site distortions and the asymmetric first peak does in fact reflect the existence of a range of distortions. Increasing the Co²⁺ concentration would result in the formation of a distinct but similar type of Co²⁺ site in the glass and the formation of characteristic Co²⁺ sites is apparent in the *symmetric* nearest neighbour peak in figure 2. Glasses 2 and 3 (see figure 2) show a sudden decrease in RSF amplitude at distances $> 4\text{ Å}$. Such decreases in RSF amplitude beyond distances

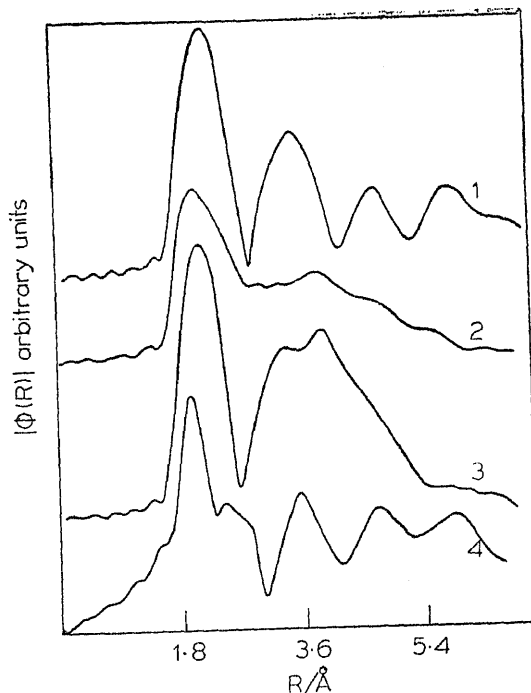


Figure 2. RSF's of cobalt oxide glasses. The numbers indicate the following molar compositions (1) $\text{ZnSO}_4:\text{Na}_2\text{SO}_4:\text{K}_2\text{SO}_4:\text{CoSO}_4::15:30:30:25$ (2) $25:25:25:25$, (3) $20:20:20:40$ and (4) $\text{CoO}:\text{B}_2\text{O}_3::20:80$.

of metallic glasses where dense random-close-packing models are valid (Wong 1980). In glass 1, however, the decrease in RSF amplitude for $R > 4\text{\AA}$ is not so significant and peaks are discernible to $5.5\text{\AA}$. It may be recalled that these distances in glass 1 are attributed to Co-Zn or to Co-Co. The decreased structure in the RSF due to increasing Co^{2+} concentration, allows for two possible explanations. One is that the scattering amplitude of Co^{2+} ions is predominant and that scatterers further away than the "line-of-sight" Co^{2+} scatterers are consequently screened. The RSF in this case will then show only the presence of atoms in between the absorber Co^{2+} and the "line-of-sight" Co^{2+} scatterer. The other explanation could be that the formation of typical Co^{2+} sites in glasses containing higher concentrations of Co^{2+} gives rise to an intrinsically less structured RSF and this may obscure features due to Co^{2+} in Zn^{2+} sites typical of dilute glasses.

3.2b. Borate glass The noise level in the EXAFS of the borate glass is considerably high (note the high background level in the RSF for $R < 1.5\text{\AA}$). The nearest neighbour peak at $1.90\text{\AA}$ (the Co-O distance) (which was merely asymmetric in the sulphate glasses) is now resolved into two distinct components. The sharpness of the first peak at the normal Co-O distance, indicates the presence of a single structural unit. The peak at $2.70\text{\AA}$ has a rather large width and indi-

4. Conclusion

In brief, the Co^{2+} site symmetry in ionic and in covalent glasses appears to be very similar to that in the rare earth cobaltites. This rather interesting feature may ensure from the characteristic O^{2-} ligancy of the Co^{2+} ions. Further, structural information from EXAFS (related to the structuredness of the RSF) appears to be reduced in the presence of a higher concentration of scatterers. The origin of this effect is, however, not known.

Acknowledgements

The authors are grateful to Professor C N R Rao, who suggested the possibility of using probe ion EXAFS for structural studies, for his encouragement and for helpful discussions. Thanks are due to Dr W H Madhusudan for assistance in the preparation of the cobaltites.

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Electrical conductivity studies in sulphate glasses and the mixed alkali effect †

H G K SUNDAR and K J RAO*

Solid State and Structural Chemistry Unit, Indian Institute of Science,
Bangalore 560 012, India

MS received 31 December 1981

Abstract. Electrical conductivities of alkali sulphate-zinc sulphate glasses have been measured. The variation of conductivity with composition confirms the presence of the mixed alkali effect. The origin of mixed alkali effect has been explained on the basis of structural considerations reported earlier by us.

Keywords. Ionic glasses ; conductivity ; mixed alkali effect.

Introduction

In an earlier paper (Rao and Sundar 1980) on conductivity of sulphate glasses, we reported the mixed alkali effect in K_2SO_4 - Na_2SO_4 - $ZnSO_4$ glasses. We had attributed the effect to a structural origin using a viable structural model for sulphate glasses. Microscopic strain fields develop around the Na^+ ions and it could account for the observed conductivity minimum. We therefore considered it imperative to examine how other alkali ions behave in mixed alkali compositions of sulphate glasses. In this paper, the observation of the mixed alkali effect for two other alkali pairs is reported and the general conductivity expression suggested earlier is found to be adequate to account for the mixed alkali effect.

Experimental

Glasses were prepared using $ZnSO_4 \cdot 7H_2O$, K_2SO_4 (BDH) and Rb_2SO_4 or Cs_2SO_4 (Merck) samples with a minimum purity of 99% as batch materials. Batches weighing 5-10 g were melted in platinum crucibles in an electric furnace and samples suitable for conductivity measurements were obtained as described earlier (Narasimham and Rao 1978, Sundar and Rao 1980). The conductivity cell and the measuring technique have also been discussed earlier (Narasimham *et al*

Keithley electrometer) through the sample for a known applied voltage (5 V). The current was passed only for very brief periods (less than 30 sec at a time) in order to avoid polarization. In the present studies also conductivities were measured beyond the glass transition and upto temperatures where the samples either deform under the spring loaded electrodes or crystallised, thus rendering further measurements inaccurate. All the glasses were annealed at a temperature 10 K below T_g before final measurements of σ were made.

3. Results and discussion

The conventional plots of $\log \sigma$ vs T^{-1} are given for various glasses in figure 1. For clarity actual points have not been shown in the conductivity plots. The glasses exhibit an inflection point which corresponds to the glass transition temperature. Variation of conductivity (σ), activation energy (E_a) and the limiting conductivity (σ_0) are plotted separately for Rb and Cs glasses in figures 2 and 3.

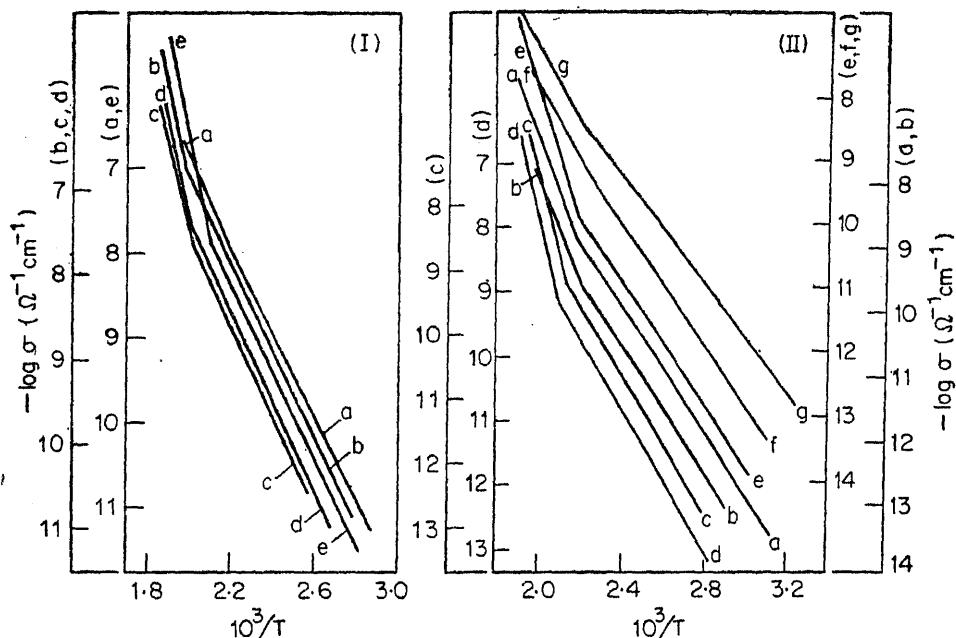


Figure 1. Variation of conductivity with temperature.

I 50% ZnSO_4

II 60% ZnSO_4

(a) 45% K_2SO_4 5% Rb_2SO_4

(a) 35% K_2SO_4 5% Cs_2SO_4

(b) 35% K_2SO_4 15% Rb_2SO_4

(b) 30% K_2SO_4 10% Cs_2SO_4

(c) 25% K_2SO_4 25% Rb_2SO_4

(c) 25% K_2SO_4 15% Cs_2SO_4

(d) 20% K_2SO_4 30% Rb_2SO_4

(d) 20% K_2SO_4 20% Cs_2SO_4

(e) 15% K_2SO_4 35% Rb_2SO_4

(e) 15% K_2SO_4 25% Cs_2SO_4

The relevant quantities for the pure K_2SO_4 - $ZnSO_4$ glasses were taken from earlier work (Narasimham *et al* 1979). The percentages of $ZnSO_4$ in K-Rb-Zn and K-Cs-Zn glasses were 50% and 60% respectively since these formed very stable glasses. The activation energies and $\log \sigma_0$ values for Zn (Rb, K) SO_4 glass exhibit no variation in the entire composition range. The behaviour of these quantities in Zn (K, Cs) SO_4 glasses exhibited considerable scatter but with an average which had little variation. The conductivity variations in figures 2 and 3 clearly establish the occurrence of the mixed alkali effect in ionic sulphate glasses. In the structural model of sulphate glasses considered in our earlier study K^+ ions are co-ordinated to four sulphate ions. The occupation of K^+ ion sites by smaller Na^+ ions causes a small degree of inward pull of the surrounding ions

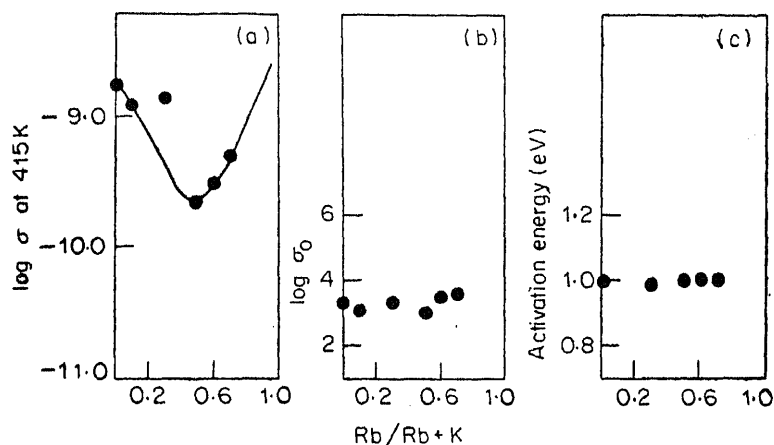
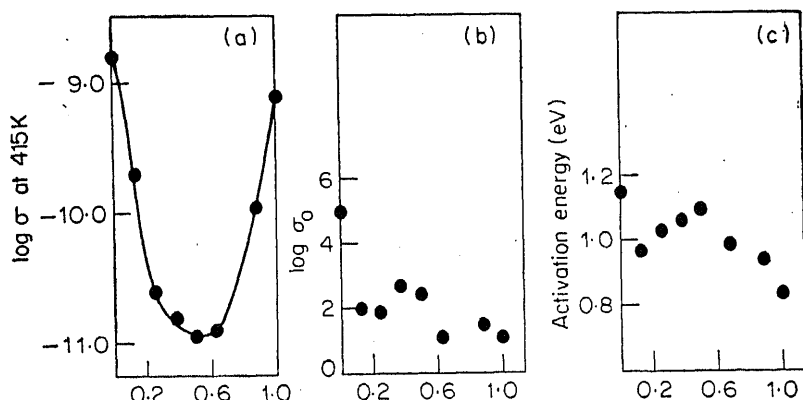


Figure 2. Variation of (a) $\log \sigma$, (b) $\log \sigma_0$ and (c) activation energy due to mixed alkali effect in $50 ZnSO_4 \cdot x K_2SO_4 \cdot (50 - x) Rb_2SO_4$ glasses.



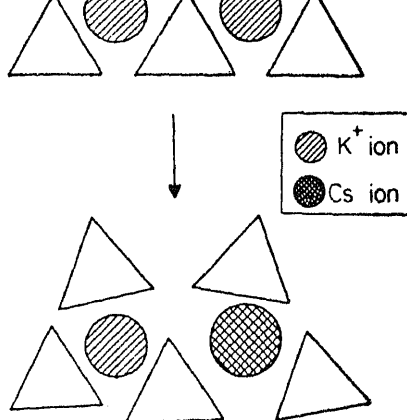


Figure 4. Schematic of possible rearrangement of structure when a K^+ ion is substituted by larger Cs^+ ion. Note that diffusion outwards is difficult when the larger ion is present.

and hence creates a local strain field. This strain field has the effect of locking up the K^+ ions in the neighbourhood which, we assumed, would therefore not contribute to conductivity. Since the substitution of Na^+ ions in general leads to a decrease in volume, there is an average enhancement of activation barriers. The contribution of Zn^{2+} ions to conductivity was neglected throughout.

Similar considerations may be applied to the other alkali pairs though we do not have a clear idea of the nature of the co-ordination of Cs^+ or Rb^+ ions. Substitution of K^+ ions by larger ions may not, in general, affect the activation energy since the anions can rearrange with no net strain when pushed outwards. We assume therefore, that the activation energies are unmodified. However, the K^+ ions in the immediate neighbourhood of larger (Rb^+ or Cs^+) ions are still locked up as schematically represented in figure 4 in two dimensions. The fact that activation energies and the pre-exponential terms are not much affected is borne out in figures 2 and 3.

Hence, the conductivity variation is only due to the locking up of a fraction of dissimilar alkali-ion pairs which are nearest neighbours. We can therefore represent the total conductivity σ_t of a $xZnSO_4(1-x)[f(Rb, Cs)_2SO_4(1-f)K_2SO_4]$ glass by the expression,

$$\begin{aligned} \sigma_t = & (1-x) A_{zn^{2+}} \cdot \exp \left[\frac{-E_{zn^{2+}}}{RT} \right] + 2(1-x)(1-f) A_{k^+} \exp \left[\frac{-E_{k^+}}{RT} \right] \\ & + 2(1-x)f A_{rb^+/cs^+} \cdot \exp \left[\frac{-E_{rb^+/cs^+}}{RT} \right] \\ & - 4(1-x)^2(1-f)f A_{k^+} \cdot \exp \left[\frac{-E_{k^+}}{RT} \right] \end{aligned} \quad (1)$$

A 's and E 's represent the respective pre-exponential (frequency) factor and activation barriers.

The last term represents the contribution from locked-up K^+ ions whose concentration is governed by the joint probability of the presence of K^+ and the other alkali ion as immediate neighbours. Assuming that

$$A_{Rb^+/Cs^+} \cdot \exp\left[\frac{-E_{Rb^+/Cs^+}}{RT}\right] \cong A_{K^+} \exp\frac{-E_{K^+}}{RT}$$

in view of figure 2. Thus the value of f corresponding to the minimum conductivity may be obtained by differentiating equation (1) with respect to f ,

$$\frac{\partial \sigma_t}{\partial f} = 0 \simeq \exp\left[\frac{-E}{RT}\right] \{-2(1-x)A + 2(1-x)A - 4A(1-x)^2(1-2f)\} = 0$$

or

$$2(1-x)(1-2f) \simeq 0; \text{ or } f \simeq \frac{1}{2}$$

The value of f obtained is in agreement with the conductivity behaviour in figures 2 and 3. The unique size ratio of K^+ to O^{2-} is the factor which, while causing significant strain contributions when Na^+ is present, does not affect the activation barriers when larger alkali ions are present. We therefore feel that in ionic glasses the mixed alkali effect is primarily a structural consequence and conductivity is dominantly affected by packing considerations, perhaps unlike in other network and covalently bonded glasses (Isard 1969, Day 1976)

Acknowledgements

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Reactions of co-ordinated ligands : Kinetics and mechanisms in the charge transfer interaction between dichloro or diaquo triethylene tetramine Co(III) and ferrocyanide

G VISALAKSHI and K S VENKATESWARLU*

Reactor Chemistry Section, Chemical group, Bhabha Atomic Research Centre, Bombay 400 085, India

MS received 8 November 1980 ; revised 7 April 1982

Abstract. The cherry red-coloured solid state product obtained by the reaction of *cis-a* diaquo Co(III) triethylene tetramine with ferrocyanide was examined by thermogravimetric, infrared and Mössbauer techniques. Its electronic spectrum in aqueous medium was interpreted to consist of charge transfer IT transition at 440 nm and a ligand field transition around 330 nm. The kinetics of formation of this 1:1 product in solution was also studied.

Keywords. *Cis-a* diaquo Co(III) triethylene tetramine ; charge transfer IT transition ; kinetics of formation.

1. Introduction

In recent years there has been increasing interest in intranuclear electron transfer processes especially for identifying and isolating long-lived dinuclear intermediates. The studies by Jwo and Haim (1976) and those of Haim and Sutin (1976) are typical examples wherein complex ferrocyanides were employed. If the dinuclear complex is to be long-lived, the thermal electron transfer reaction should be preferably absent or be very slow. This paper presents the isolation of a cherry red dinuclear complex formed in the reaction between *cis-a* diaquo Co(III) triethylene tetramine and ferrocyanide, and a study of its behaviour.

2. Experimental

2.1. Preparation

The cherry red complex was prepared as follows : The *cis-a* dichloro Co(III) triethylene tetramine complex was prepared and purified according to the method suggested by Sargeson and Searle 1967. The *cis-a* diaquo complex was prepared by dissolving the

*To whom correspondence should be made.

dichloro complex in water and allowing it to stand for 24 hr for aquation. When the aquo complex was mixed with aqueous solution of $K_4Fe(CN)_6$ a cherry red colour was immediately formed. This solution showed an electronic absorption at 440 nm and a pH between 7 and 8. Equal volumes of equimolar solution of the two reactants were mixed and allowed to stand for an hour at room temperature with occasional stirring. On adding ethanol and keeping under refrigeration, bright cherry red solid separated out. After filtering, the solid was repeatedly washed with ice-cold ethanol and dried under vacuum in a desiccator.

2.2. Chemical analysis

The solid was dissolved by heating first with nitric acid, then with perchloric acid and finally with sulphuric acid. The K, Co and Fe content was determined by standard analytical techniques. K was determined by flame photometric method. Fe and Co were estimated spectrophotometrically by ortho phenanthroline (Vogel 1961) and nitroso-R-salt (Sandell 1959) methods respectively.

2.3. Instrumental

A Perkin-Elmer IR spectrophotometer was employed for recording the IR spectra of the sample using hexachloro butadiene as the mulling agent. A Stanton TG balance with a sample size of 400 mg and a heating rate of $6 K min^{-1}$ in static air was employed. Electronic spectra were recorded with a Hitachi Model spectrophotometer. A home-made constant acceleration Mössbauer spectrometer using 3 mci Co-57 (pd) in conjunction with an MCA was used to record the ^{57}Fe Mössbauer spectra of the solid.

3. Results and discussion

The results of chemical analysis of the cherry red solid for Fe, Co and K content (table 1) show a reasonable fit for the molecular formula $K_4Co(Fe(CN)_6)_3 \cdot 4H_2O$ consistent with the expectation from the route followed for its synthesis.

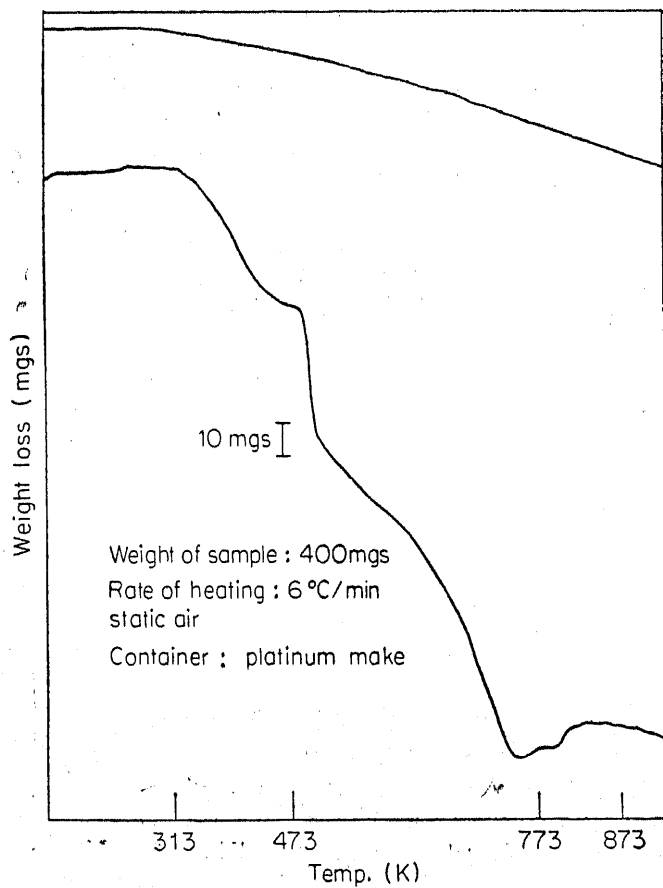
The cherry red complex on dissolution in water satisfies Beer's law. The molar extinction coefficient is $1000 \text{ litre mole}^{-1} \text{ cm}^{-1}$ and its stoichiometry is found to

Table 1. Results of chemical analysis of cherry red solid.

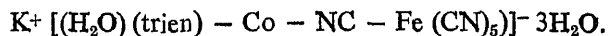
Element	Weight (%)	
	Observed	Calculated
K	7.4	7.4
Fe	10.5	10.6

be 1:1 by 500's method of continuous variation and molar ratio method. These results support the above-mentioned molecular formula for the complex arrived at from chemical analysis. Its stability constant was found to be 4.5×10^5 litre mole⁻¹. To ascertain whether the colour of the complex is vested in the cationic or anionic moiety of the solid, its solution was passed through the Na form of a cationic exchanger, which did not retain the colour. The moiety can either be neutral or anionic in nature. A similar treatment with the chloride form of an anionic exchanger resulted in the retention of the colour on the exchanger proving that the moiety responsible for the colour is anionic in nature.

The TG analysis of the cherry red complex was performed with the object of probing the thermal stability of the solid complex as well as to determine if all the four molecules of water are bound equally strongly from its dehydration behaviour. The observed TG run is given in figure 1. The thermogram shows a very slow and gradual loss in weight in the temperature interval 313-873 K with a superposed very sharp loss in weight around 480 K. The overall loss in weight between 313-873 K accounts for loss of one molecule of trien and four molecules of H₂O. However, if one calculates the loss in weight represented by the steep loss alone,



pared to the fourth in the solid state, i.e., structurally there are two kinds of water molecules in 3 to 1 ratio. Considering that ferrocyanide was used as the starting material and in the light of the TG and ion exchange results mentioned above, the following structural units are proposed for the cherry red complex.

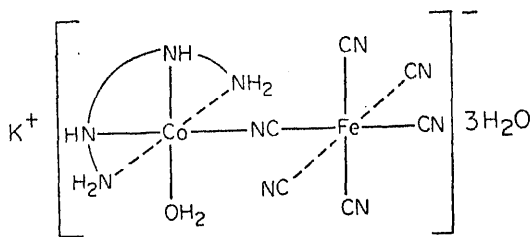


This does not disturb the ferrocyanide unit and involves a single linear CN bridge, which is well documented as far as cyanides are concerned.

This type of structural unit gets independent support from IR results. The IR spectrum shows an absorption at 2040 cm^{-1} with a clear shoulder at 2100 cm^{-1} . The former is attributed to stretching of terminal CN groups whereas the latter comes from that of bridging $\text{C}\equiv\text{N}$ groups (Nakamoto 1963). A band at 585 cm^{-1} attributable to Fe-C stretching in ferrocyanide was also observed in the IR spectrum of the cherry red solid.

It is reported (Nakamoto 1963) that in solids both co-ordinated as well as lattice water molecules give characteristic IR absorption in the range $3550\text{--}3200\text{ cm}^{-1}$ (due to antisymmetric and symmetric O-H stretching) and also in the range $1630\text{--}1600\text{ cm}^{-1}$ (due to H-O-H bending). On the other hand, the co-ordinated H_2O molecules give an additional absorption in the region $880\text{--}650\text{ cm}^{-1}$ due to rocking mode of the water molecule. In the IR spectrum of our complex at room temperature, there are absorptions in the neighbourhood of 3000 cm^{-1} and 1600 cm^{-1} in addition to several sharp ones in the range $600\text{--}850\text{ cm}^{-1}$. It is difficult to unequivocally discern the absorption arising out of rocking modes of H_2O in this group of peaks. The spectrum in this $600\text{--}850\text{ cm}^{-1}$ region remains unaffected after heating the sample at 473 K , i.e., after the steep loss of $3\text{H}_2\text{O}$ molecules, as indicated by the TG scan. It implies that the lone co-ordinated water molecule is lost after 473 K .

The foregoing results enable us to propose the following structure for the cherry red complex.



In order to investigate the origin of colour of this cherry red complex, the electronic spectra of solution of the complex in water with different concentrations were taken. The spectra are shown in figure 2. Two well-defined maxima at 330 and 440 nm were observed. Vogler and Kunkely (1975) have reported the electronic spectra of dinuclear complex $[(\text{CN})_5\text{Co(III)NCFe(II)(CN)}_5]^{6-}$ as having two maxima at 326 and 385 nm . They assigned the 326 nm band to Co(III) ligand field separation, and the 385 nm band to intervalence charge transfer process involving the two cations. On the same lines, in our case, the 440 nm

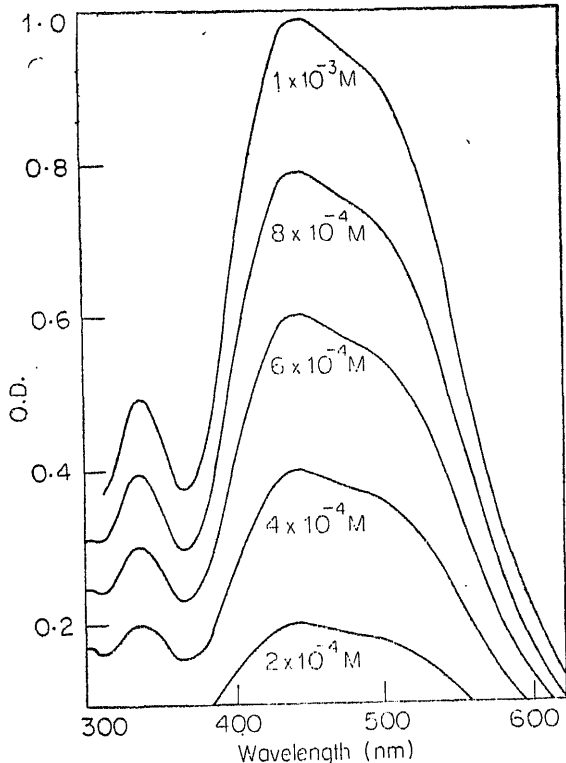


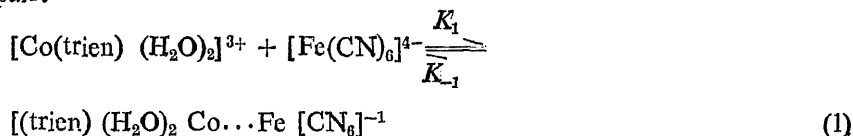
Figure 2. Absorption spectra of solutions obtained by the dissolution of different amounts of cherry red solid in water.

band is assigned to charge transfer involving the interaction of the two metals of the anionic species. The 330 nm band is assigned to the Co(III) ligand field. According to the qualitative potential energy diagram constructed by Vogler and Kunkely (1975), the 440 nm band observed here represents a spin allowed intervalence transition.

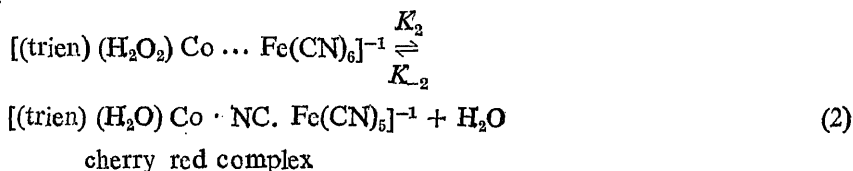
It would be worthwhile and interesting to probe the extent of electron transfer in these charge transfer complexes. A bulk magnetic susceptibility measurement would not be a very sensitive tool to do this since such a transfer is very small in practice and the macroscopic measurement could not detect it. A microscopic technique which looks more closely at either cobalt(III) or iron (II) site is desirable. At least for iron site, it was felt that Mössbauer might throw some light on the situation.

It is well-known that the two extreme situations in which the 6th *d* electron of Fe either stays on it or goes over to Co completely far away from it can be easily distinguished by Mössbauer spectroscopy from different isomer shifts observed for Fe(II) and Fe(III) cases. With this in mind, we recorded the ^{57}Fe Mössbauer spectra of the cherry red complex and to our surprise observed that

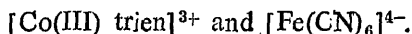
The first step in the formation of the cherry red complex is the constitution of an ion-pair.



The rate of formation of this ion-pair is very fast, so that K_{-1} compared to K_1 can be neglected in practice. If this ion-pair gives the final cherry red product through a unimolecular reaction, the next step can be logically visualised as follows :



The slowest step in this process is the removal of water molecule and hence it is the rate-determining step. The overall reaction rate depends on the concentration of the ion-pair, which in turn depends on the concentration of the starting ions, viz.,



The rate expression may then be written as

$$dc/dt = K [\text{Co}(\text{trien}) (\text{H}_2\text{O})_2]^{3+} [\text{Fe} (\text{CN})_6]^{4-} \quad (3)$$

where $K = K_1 K_2 / (K_1 + K_2)$.

Data pertaining to kinetic studies namely values for OD at 440 nm vs time plots presented in figure 3 show that in diaquo complex, it is difficult to resolve the semilog plots. In order to investigate if the two $t_{1/2}$'s can be resolved, the starting diaquo complex of cobalt was replaced by the corresponding dichloro complex of cobalt. The resulting kinetic data plotted in figure 3 also show that for dichloro Co (III) trien complex the semilog plots are resolvable into two linear components having distinct $t_{1/2}$ values. This clearly shows that in dichloro complex its aquation takes place prior to the interaction with ferrocyanide.

A linear plot of dc/dt (figure 4) against the product of concentrations of the reactants indicates an overall second order kinetics. The reaction rate and $t_{1/2}$ for the system [9×10^{-4} M Co(III) trien complex and 9×10^{-4} M ferrocyanide] were measured at temperatures 301, 308, 318 and 333 K to estimate E_a , the activation energy of the reaction. A linear plot of $\log K$ vs $1/T$ was obtained. The activation energy for the interaction of cis- α diaquo Co(III) trien complex with ferrocyanide was found to be 28.8 kJ.

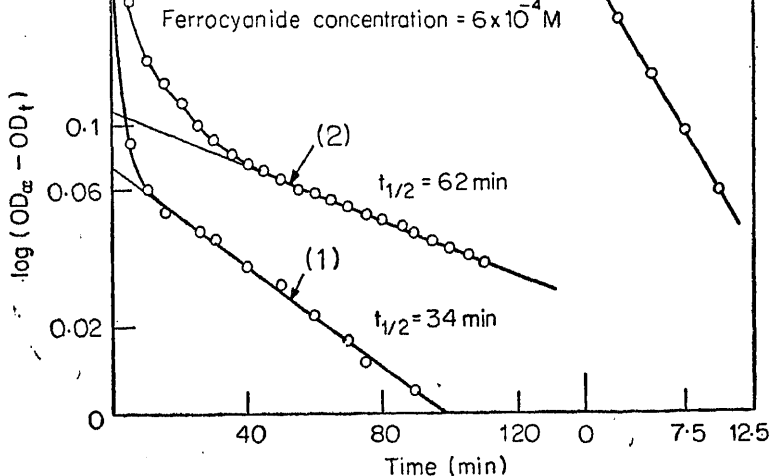


Figure 3. Plot of $\log (OD_{\infty} - OD_t)$ vs. time for *cis-a* diaquo/dichloro cobalt(III) trien complex and ferrocyanide system. Curve (1) diaquo cobalt(III) complex and ferrocyanide system. Curve (2) dichloro cobalt(III) complex and ferrocyanide system.

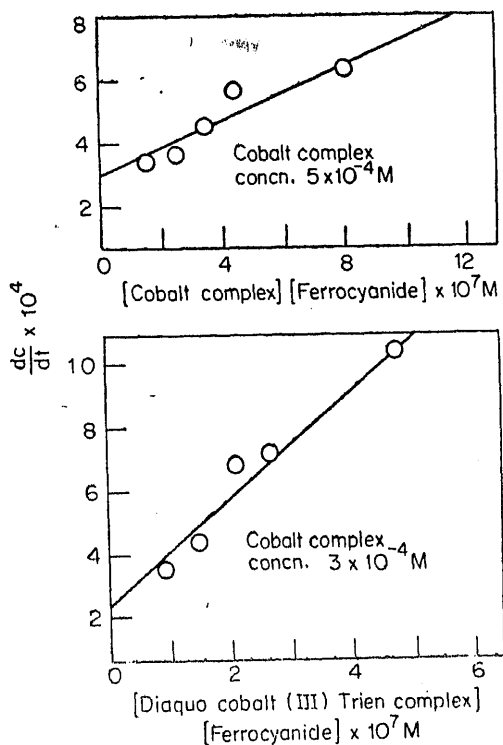


Figure 4. Plot of dc/dt vs. [Diaquo Co(III)trien complex] [Ferrocyanide].

CNDO calculations of N-methyl substituted acrylamides

G RAMANA RAO

Department of Physics, University College, Kakatiya University, Vidyaranyaपुरi, Warangal 506 009, India

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Abstract. CNDO calculation is made for N-methyl acrylamide (both in *cis* and *trans* configurations) and N,N-dimethyl acrylamide. The charges, bond orders and dipole moments are discussed and compared with those of acrylamide. The *trans* form of N-methyl acrylamide is found to be more stable than *cis* isomer by 4.5 kcal/mole.

Keywords. CNDO calculation; acrylamides; dipole moments; bond orders.

Introduction

It is well known that in amide molecules, no single valence bond structure is consistent with all their properties. This is due to the delocalization of the carbonyl π -electrons and lone pair electrons of nitrogen, resulting in the partial double bond character of the C-N bond (Morris and Orville Thomas 1961; Annon 1955, 1956; Venkata Chalapathi and Venkata Ramiah 1968, 1971). N-methyl substituted acrylamides, in addition to nitrogen lone pair, ethylenic electrons also take part in such conjugation. The effect of such conjugation has been studied in the case of acrylamide (AC) by CNDO method (Ramana Rao and Venkata Ramiah 1975). The aim of the present paper is to make similar studies on N-methyl acrylamide (NMAC) and N,N-dimethyl acrylamide (DMAC) and to examine the effect of the above conjugation as well as the effect of N-methylation in AC on charge distributions, bond orders, dipole moments and barriers to internal rotation about the C-N bond.

Method of calculation

The CNDO/2 calculations (Pople and Beveridge 1971) of AC, NMAC (both *cis* and *trans* forms) and DMAC are accomplished by programme QCPE 142 (CNDO (Dobosh)). The structure of the molecules is presented in figure 1. The structure parameters used are $r(C=C) = 1.337 \text{ \AA}$, $r(C=O) = 1.243 \text{ \AA}$, $r(C-N) = 1.315 \text{ \AA}$, $r(C-C) = 1.47 \text{ \AA}$, $r(N-H) = 1.02 \text{ \AA}$, $r(N-C) = 1.47 \text{ \AA}$,

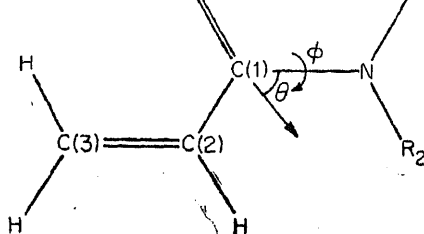


Figure 1. Structure of acrylamide ($R_1 = R_2 = \text{H}$), N-methylacrylamide ($R_1 = \text{CH}_3$, $R_2 = \text{H}$) and N,N-dimethylacrylamide ($R_1 = R_2 = \text{CH}_3$) θ is the angle the dipole-moment makes with C-N bond and ϕ is the angle of rotation of amino group from the rest of the molecular plane.

are assumed to be 120° each. The atomic orbitals used in the calculations are $1s$ for hydrogen, $2s$, $2p$ for carbon, nitrogen and oxygen.

3. Results and discussion

3.1 Charges, bond orders and dipole moments

The total charge ($\pi + \sigma$), net pi-charge and mobile bond orders of NMAC and DMAC are presented in table 1. The results of AC are given for comparison.

The net total charges on oxygen, functional carbon and nitrogen in AC are $-0.371e$, $+0.358e$ and $-0.241e$ respectively. On successive methylation of AC, the net total charges on oxygen and functional carbon atoms remain almost unaltered whereas that on nitrogen atom shows a considerable decrease in magnitude as can be seen from table 1. The total charge in the amide system (*i.e.*, peptide bond) in AC, NMAC and DMAC is $-0.254e$, $-0.212e$ and $-0.179e$ respectively. Thus the net total charge in the peptide bond is negative and the magnitude of the charge decreases with successive methylation of AC. This result is in agreement with that reported for primary, secondary and tertiary amides (Yan *et al* 1970).

In AC, NMAC and DMAC the pi-bonding between nitrogen lone pair and carbonyl group results in de-localization of nitrogen lone pair electrons. The pi-orbitals of ethylenic bond also take part in such a conjugation. The net pi-charge on nitrogen atom is $0.185e$ in AC. The corresponding charge in NMAC and DMAC on nitrogen atom is $0.218e$ and $0.249e$ respectively. Thus we observe that the de-localization of nitrogen lone pair increases with successive methylation of AC. However, the sigma charge (this is the total charge minus net pi-charge) on nitrogen atom remained almost constant.

The vinyl substitution results in a small amount of pi-charge of about $0.036e$ being transferred from the ethylenic bond to carbonyl bond in AC which remains unaltered on successive methylation of AC. On the other hand, the carbonyl bond receives quite a large amount of pi-charge from nitrogen lone pair, the amount of charge being $0.185e$, $0.218e$ and $0.245e$ in AC, NMAC and DMAC respectively. Hence in acrylamide the nitrogen lone pair charge plays a dominant

Table 1. Charges* and mobile bond orders of the molecules

Molecule	Net total charges ($\pi + \sigma$)						Net π -charges			Mobile bond orders			
	O	C(1)	N	C(2)	C(3)	O	C(1)	N	C(2)	C(3)	C=O	C-N	C-C
acrylamide	-371	358	-241	-65	15	-430	209	185	-29	65	0.808	0.464	0.283
N-methyl acrylamide (<i>trans</i>)	-374	353	-191	-67	15	-431	201	218	-27	63	0.805	0.467	0.284
N-methyl acrylamide (<i>cis</i>)	-384	360	-188	-61	11	-432	204	218	-26	62	0.805	0.467	0.283
N,N-dimethyl acrylamide	-374	347	-152	-69	14	-426	193	249	-29	63	0.805	0.466	0.283

* Charges are given in the units of 10^{-3} of electronic charge.

those of the related amide molecules. As such, the vinyl substitution does not have much effect on the amide system. This agrees with the result already obtained on the basis of normal coordinates analyses (Ramana Rao and Venkata Ramiah 1981).

The mobile bond orders of these molecules are also shown in table 1. The C-N and C-C bond orders have considerable double bond character whereas C=O and C=C have reduced double bond character. This is because the carbonyl bond receives π -charge both from nitrogen lone pair and ethylenic π -bond. The bond orders of C-N and C=O are close to the values reported for formamide (Pople and Segal 1966). Further, the bond orders of three molecules considered are almost the same.

The calculated dipole moments for AC, NMAC (*trans*), NMAC (*cis*) and DMAC are 3.81, 3.80, 3.71 and 3.63 debyes respectively with corresponding directions (as shown in figure 1) as 54° , $55^\circ 24'$, $55^\circ 33'$ and $55^\circ 10'$. These values are close to one another and are also comparable to those of formamide and acetamide which are 3.71 and 3.82 debyes respectively (Yan *et al* 1970).

3.2 Barrier to internal rotation and *cis-trans* isomerism

By assuming the transition state to correspond to $\phi = 90^\circ$ (see figure 1) in accordance with the findings in the case of alkyl substituted amides (Yan *et al* 1970), the barrier to internal rotation about C-N bond of AC, NMAC and DMAC have been calculated to be 20, 17.5 and 11 kcal/mole respectively. The experimental value of barrier height in DMAC is 16.8 kcal/mole (Rogers and Woodbrey 1962). The barrier heights in formamide, N-methyl formamide and N,N-dimethyl formamide are calculated to be 20.3, 18.5 and 15.03 kcal/mole respectively by CNDO/2 method (Yan *et al* 1970). The corresponding experimental values are 19.2, 18.05 and 21 kcal/mole (Stewart and Siddal 1970). One can see that on successive methyl substitution the calculated barriers have decreased in acrylamides and also formamides. Further, the calculated values of barriers in N,N-dimethylamides are lower than the experimental values.

The charge density in the lone pair orbital of nitrogen in the ground state ($\phi = 0^\circ$) is 1.815e, 1.782e and 1.762e in AC, NMAC and DMAC. The corresponding quantities in the transition state ($\phi = 90^\circ$) are 1.966e, 1.935e and 1.904e. That is the lone pair charge is getting localized in the transition state as it increases to a value close to 2e from a value around 1.8e in the ground state. This shows that the de-localization of nitrogen lone pair is responsible for the barrier to a large extent. The same result was obtained in the case of thioamides (Srinivas Rao and Venkata Ramiah 1976).

NMAC can exist in both *cis* and *trans* forms. Our calculations show that the *trans* form of NMAC is more stable than *cis* form of NMAC by 4.5 kcal/mole.

4. Conclusions

(i) The net total charge in the partially delocalized lone pair orbital is

- (ii) The delocalization of nitrogen lone pair increases with successive methylation of AC whereas the sigma charge remains almost unaltered.
- (iii) The nitrogen lone pair charge plays an important role in determining the properties of AC, NMAC and DMAC as the pi-charge received by carbonyl bond from nitrogen lone pair is several times greater than that received from the ethylenic bond.
- (iv) The mobile bond orders of $C=O$, $C-N$, $C-C$ and $C=C$ remain almost unchanged on successive methylation in AC.
- (v) The dipole moments of AC, NMAC and DMAC are of the same magnitude as for formamide and acetamide.
- (vi) The calculated barrier heights for AC, NMAC and DMAC are found to decrease on successive methylation of AC as is the case with formamide series. The *trans* form of NMAC is found to be more stable than the *cis* form of NMAC by 4.5 kcal/mole.

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Red edge excitation and proton association in the excited state of acridine

P GANGOLA,* N B JOSHI and D D PANT

Department of Physics, DSB College, Kumaun University, Naini Tal 263 002, India

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Abstract. A comprehensive study of acridine spectra with variation of pH, wavelength of excitation, deuteration of the solvent, etc., has been made. The excited state protonation of acridine is found extra-ordinarily excitation wavelength sensitive near the red edge of the first absorption band. The proton association takes place very fast ($K_{PT} \sim 10^{10} \text{ sec}^{-1}$) on excitation at the red edge of the first absorption band (REE) and acridinium emission is observed while it is slow on short wavelength excitation (SWE). The reaction rate slows down at lower temperature which is indicated by a delay in the initiation of the effect by $\sim 8 \text{ nm}$ on REE. The acridinium type emission with REE at 80 K shows that proton tunnelling is the chief mechanism of proton transfer. The quantum yields are also found wavelength dependent. Contrary to previous observations acridinium ion also shows a REE shift at 80 K.

Keywords. Red edge excitation ; proton transfer ; acridine.

1. Introduction

Despite the well-accepted generalisation that in large molecules luminescence occurs only from the vibrationally equilibrated lowest electronic excited state, three major violations have been observed in some aromatic molecules in solutions on excitation near the red edge of the first absorption band. The first of these relates to change in polarisation of emission (Weber 1960 ; Weber and Shinitzky 1970 ; Valeur and Weber 1978), the second to a slight change in wavelength (Chen 1967 ; Fletcher 1968) and the third to a change in chemical reactivity of the excited state (Gangola *et al* 1977, 1979 ; Pande *et al* 1980 ; Shah *et al* 1980). In molecules like acridine which undergo a large change in pK value in the excited state, the rate of proton transfer changes on red edge excitation (REE). Weller (1957) who studied acridine emission with only the short wavelength excitation (SWE) did not observe any proton abstraction in alcoholic solution and reported that the rate of proton association $k \leq 1/5$ where τ is the observed

this behaviour, we present here a detailed spectroscopic study of RRB behaviour of acridine in neutral, alkaline and acidic solutions at low and room temperatures.

2. Experimental

In view of weak emission on RRB, careful attention was given to the elimination of the stray light, impurity emission—extraneous or due to ionised species of the solute and solvent Raman scattering. Spex fluorolog model 1902 has two separate double monochromators each for excitation and emission and the stray light problem was not present.

Chromatographed (courtesy CDRI, Lucknow) acridine was prepared from Fluka acridine base material and was similar to those obtained from Eastman Kodak and CIBA Research Centre, Bombay. Methanol solutions (10^{-4} M) were prepared at pH ~ 9 . Absorption, emission and excitation spectra were taken with Spex fluorolog. The spurious effect produced by Raman scattering at extreme RRB was $\sim 0.8\%$, hence was neglected. Acridinium absorption was absent even in non-alkaline solutions taken with 10 cm cell in Beckmann DK-2A spectrophotometer. The excitation spectra were taken with a more dilute solution ($\sim 10^{-5}$ M) by monitoring at 420 nm and 480 nm emission peaks respectively of SWE and RRB. The excitation spectrum of the solvent by monitoring at 480 nm (due to Raman scattering) was also obtained separately to make allowance for distortion in the actual excitation curve.

All experiments reported here are performed with the chromatographed sample mostly in methanol. If a different solvent is used in any particular experiment, it is mentioned in the text. Methanol (BDH) was used after distillation. CH_3OD (isotopic purity $> 95\%$) obtained from BARC, Bombay, was used as such. The alkalinity of the solution was varied by adding NaOH (GR grade) and H_2SO_4 (Anala R) and the pH of the solution was measured by a Phillips pH meter.

3. Results and discussion

In acidic methanol solution (pH ~ 1) only the absorption and emission spectra of acridinium are observed. The emission spectrum at 295 K is a little diffuse, however, at 80 K a well-structured spectrum is observed with a temperature blue shift of $\sim 400\text{ cm}^{-1}$. The lowest excited states of acridine are $\pi\pi^*$ (Landner and Becker 1963); ${}^1\text{L}_a$ located at 384 nm ($\epsilon_{\text{max}} - 3 \times 10^3$) slightly lower than the ${}^1\text{L}_b$, which is at 358 nm ($\epsilon_{\text{max}} - 10 \times 10^3$). The ${}^1\text{L}_a$ and ${}^1\text{L}_b$ states separate out in acridinium, the ${}^1\text{L}_a$ ($\epsilon_{\text{max}} - 3.6 \times 10^3$) band is very much red shifted while ${}^1\text{L}_b$ ($\epsilon_{\text{max}} - 17 \times 10^3$) is not displaced but intensified (figure 1). The emission and absorption spectra of acridinium agree well with those given by earlier workers (Landner and Becker 1963; Mataga *et al* 1956, 1957; Kellmann 1977; Whitten and Lee 1971). The emission spectrum at 295 K is definitely independent of excitation wavelength. However, at 80 K there is minor red shift $\sim 250\text{ cm}^{-1}$ on excitation by $\lambda_{\text{ex}} = 446\text{ nm}$ without change in the structure (figure 2). While the absence of red edge effect at 295 K is in keeping with the observation of

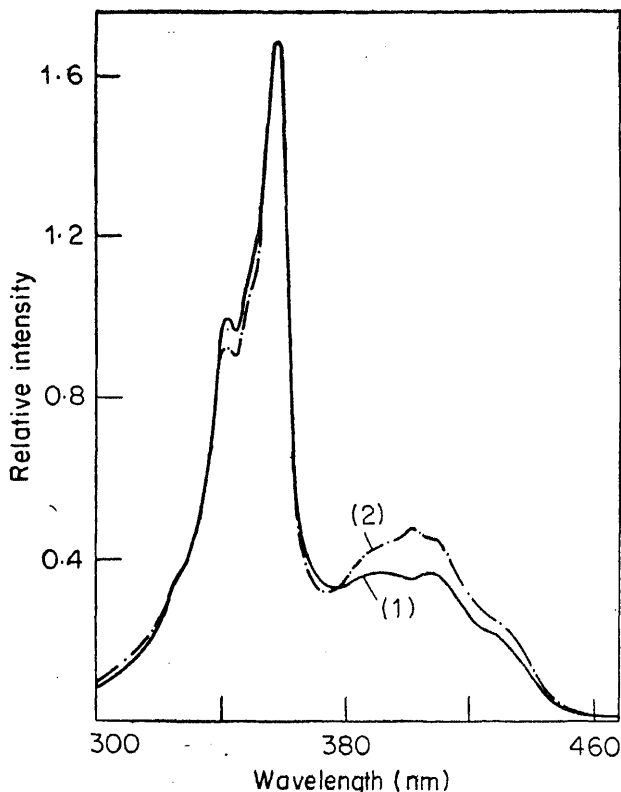


Figure 1. Absorption spectrum (1) and excitation spectrum (2) of acridinium in acidic methanol (pH $\sim$ 1) at 295 K.

Fletcher (1968), the minor red shift in acridinium emission at 80 K was not observed earlier. The magnitude of the shift and the shortest wavelength of excitation which initiates the shift appear to be pH dependent. With pH $\sim$ 0 the magnitude of the shift $\Delta\bar{\nu}$ increases to 500 cm^{-1} compared with 250 cm^{-1} at pH $\sim$ 1. The effect is discernible with $\lambda_{\text{ex}} = 440\text{ nm}$ at pH $\sim$ 0 whereas it starts with $\lambda_{\text{ex}} = 446\text{ nm}$ at pH $\sim$ 1. The emission spectra of acridinium (pH $\sim$ 0) at 80 K for different wavelengths of excitation are given in figure 3.

At pH $\sim$ 7 absorption at longer wavelengths is absent indicating the absence of acridinium ions in the ground state and the blue fluorescence of acridine is observed. The absorption and emission spectra of acridine also agree with those given by other workers. The fluorescence bands become sharper at 80 K with a very small temperature blue shift of $\sim 100\text{ cm}^{-1}$. In this solution there is apparently no wavelength shift on RBB at 295 K as well as at 80 K, an observation

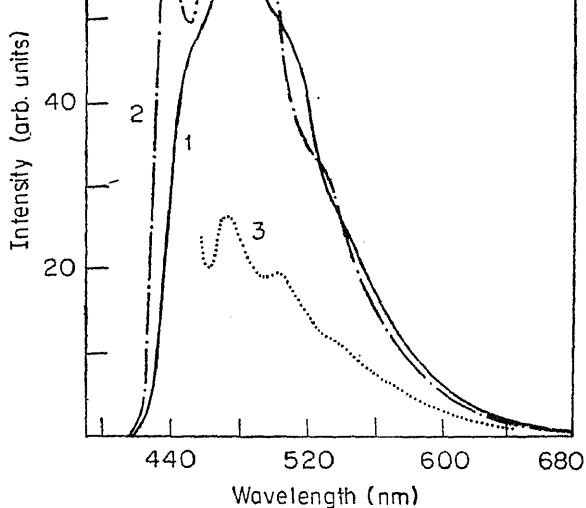


Figure 2. Emission spectra of acridinium in acidic methanol (pH $\sim$ 1) with λ_{ex} : (1) 350 nm at 295 K, (2) 350 nm at 80 K and (3) 446 nm at 80 K.

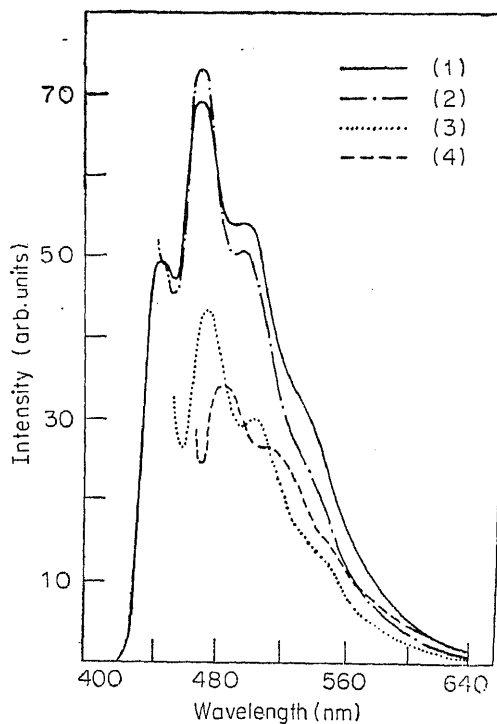


Figure 3. Emission spectra of acridinium in acidic methanol (pH $\sim$ 0) at 80 K with λ_{ex} : (1) 350 nm, (2) 430 nm, (3) 440 nm and (4) 446 nm.

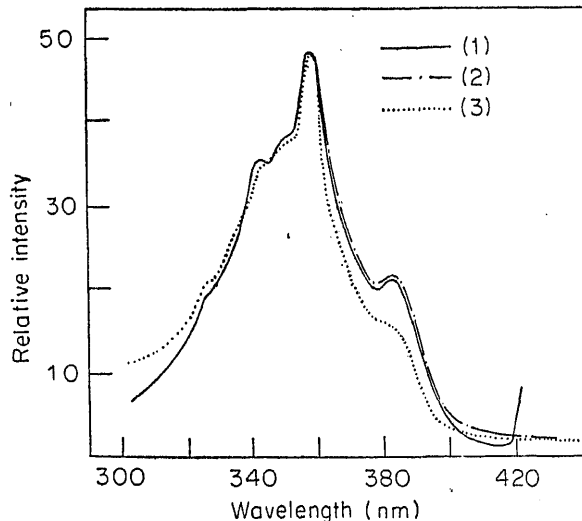


Figure 4. Excitation and absorption spectra of acridine in alkaline methanol (pH $\sim$ 9) at 295 K ; excitation spectra with emission monitored at (1) 420 nm and (2) 480 nm and (3) absorption spectrum.

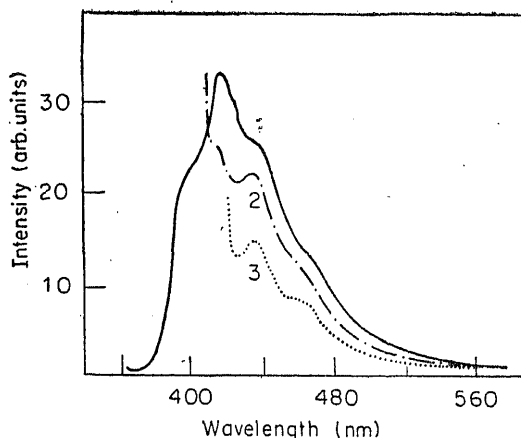


Figure 5. Emission spectra of acridine in methanol (pH $\sim$ 7) at 295 K with λ_{ex} : (1) 350 nm, (2) 440 nm and (3) 410 nm.

Around pH $\sim$ 9 in alkaline solutions in methanol or ethanol or ethanol + methanol (1 : 1), although only acridine exists in the ground state, the fluorescence emission now shows edge excitation effect definitely. On adding alkali there is not the slightest change in absorption or SWE emission spectrum of acridine but on REE acridinium type emission is observed. REE effect in the pH range 7.5 to 9.5 was investigated and acridinium emission was studied. The effect was best observed in pH range 8 to 9 after which again the relative intensity of acri-

Table 1. Excitation wavelength dependence of emission bands of acridine and acridinium at 295 K and 80 K.

	295 K	80 K
Acridine (in alkaline methanol)		
SWE ($\lambda_{ex} = 350$)	400, 420, 440, 465, 500	398, 418, 444, 468, 506, 544
REE ($\lambda_{ex} = 420$)	448, 476, 500, 535	444, 472, 500, 535
Acridinium (in acidic methanol)		
SWE ($\lambda_{ex} = 350$)	452, 480, 500	444, 470, 500, 535
REE ($\lambda_{ex} = 446$)	no change, structure improves	— 482, 515, 555

350 nm excitation (SWE) usual fluorescence of acridine is observed. On excitation with longer wavelengths around 390 nm, however, some subtle changes in the spectrum start appearing, finally leading to acridinium type emission on excitation by 415 nm. There is no further change in the structure of the spectrum on excitation with 420 nm (REE) except for an additional red shift of 100 cm^{-1} . The subtle changes appearing on excitation by $\lambda_{ex} \sim 390 \text{ nm}$ may be due to a transient state of H^+ in the solvation cage of acridine or it may be due to an admixture of acridine and acridinium spectra. The intensity ratio of 475 nm and 445 nm emission bands goes on increasing by excitation with longer wavelengths and finally beyond 415 nm excitation only the acridinium type spectrum appears. The REE spectrum of acridine at 295 K, however, has a much better resolved structure than the acridinium spectrum at the same temperature. In fact, it has the same spectral structure as the acridinium spectrum at 80 K observed on SWE with $\lambda_{max} \sim 472 \text{ nm}$ and vibronic spacing $\Delta\bar{\nu}_v \sim 1270 \text{ cm}^{-1}$.

The edge effect has also been investigated at 80 K in alkaline methanol + ethanol (1 : 1) glass. This solvent is chosen because it forms a clear and uncracked glass at 80 K, however, in alkaline methanol also similar results were obtained. At 80 K, the vibronic structure of the emission spectrum is well resolved $\Delta\bar{\nu}_v \sim 1270 \text{ cm}^{-1}$ and the edge effect can be studied carefully. Figure 7 shows the spectra obtained with alkaline methanol + ethanol (pH ~ 9) glass at 80 K. The usual acridine spectrum is observed with SWE. Perceptible change starts appearing with 403 nm excitation which is seen not as a change in the emission wavelength, but as a relative change in the intensities of the bands. On excitation with 415 nm acridinium type emission but slightly blue shifted from SWE acridinium emission is observed. Finally, with REE (420 nm) purely acridinium emission both in wavelengths of the bands and their intensity distribution is obtained. Although the complete change from acridine to acridinium spectrum is observed on REE at 420 nm both at 295 K and 80 K, the intensity change starts appearing at a shorter wavelength of excitation at 295 K. This is evident from the curve 4

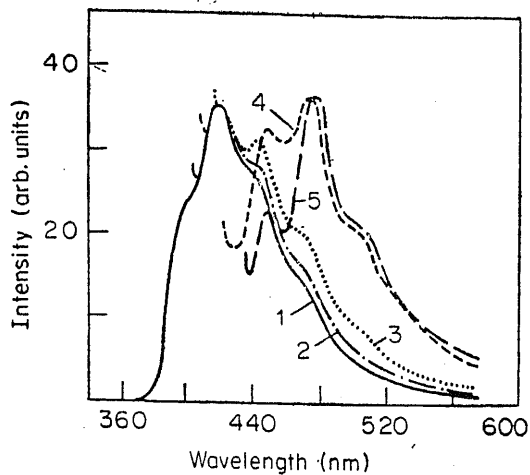
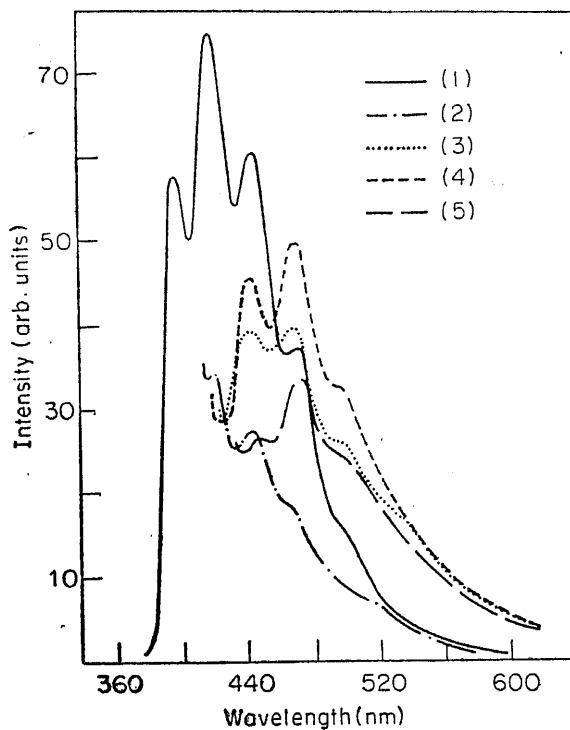


Figure 6. Emission spectra of acridine in alkaline methanol (pH $\sim$ 9) at 295 K with λ_{ex} : (1) 350 nm, (2) 395 nm ; (3) 400 nm, (4) 405 nm and (5) 420 nm.



295 K. The pH dependent wavelength effect in acridinium at 80 K may also be due to the proton transfer rate being wavelength dependent. However, for acridinium the heterogeneity of the emitters might cause similar effect. On the other hand, it is also known that the presence of other H^+ or OH^- ions greatly affects the hydrogen bonding or ion-pair formation (Zundal 1976).

Deuterium effect at 190 K was observed in CH_3OD alkaline solution. With SWE the spectra are identical in wavelength and intensity distribution in both CH_3OH and CH_3OD solutions and the emission is due to acridine. Intensity changes on REE at 190 K appeared to be slower in CH_3OD solution. However, some uncertainty existed in the pH value of CH_3OD which did not allow a careful assessment of deuterium effect. At 295 K, however, the two spectra were identical on REE. We believe that the rate of proton transfer becomes faster at 295 K and the solvent isotope effect is discernible only at low temperature.

The acridinium excitation and absorption spectra are given in figure 1. The absorption and excitation spectra agree almost quantitatively in short wavelength region, however, in the long wavelength transition the quantum yield increases by about 34%. The excitation and absorption spectra for acridine in alkaline methanol solution are given in figure 4. Here again there is an increase of 34% in the quantum yield value for long wavelength transition. On the long wavelength part (REE), however, the excitation curve 1 monitored at 420 nm (acridine emission peak) goes below, while the curve 2 monitored at 480 nm (acridinium emission peak) passes above the absorption curve. Normally one should have expected both the excitation curves to lie above the absorption curve as the quantum yield for long wavelength transition, i.e., 1L_a is higher. The fall in quantum yield as seen by curve 1 clearly indicates that acridine is being converted into acridinium in the excited state. The quantum yields (ϕ) for acridine and acridinium (as measured in aqueous solutions on $\lambda_{ex} = 350$ nm) are 0.38 and 0.55 respectively, i.e. ϕ_{AH} is higher by 44.7% than ϕ_A . Calculated on this basis, if acridinium is being formed in the excited state by REE, curve 2 should reveal a further increase of 44.7% over the initial 34%, thus a total increase of 93.9% should be observed. Quantitative measurements from enlarged curves show that the total increase in ϕ revealed by the excitation curve monitored at 480 nm is $\sim 93\%$ near the long wavelength region, although error in these experiments is large ($\sim 20\%$). Thus we believe that these results though only semiquantitative can be explained if acridinium is formed in the excited state. The absence of red edge effect at pH ~ 7 and its observation at pH ~ 9 also rules out the presence of acridinium in the ground state to be the origin of the effect.

The nitrogen of aza-anthracene becomes highly basic on excitation. However, Weller on excitation with 365 nm did not observe any change in acridine emission although an excited state protonation was expected. Weller ascribed the failure of proton association to slow rate of reaction ($K_{PT} \sim 10^6 \text{ sec}^{-1}$) compared to the lifetime of acridine molecule (16 ns). Our results obtained on REE, however, suggest that the protonation reaction increases around 400 nm, and around 410 nm the reaction is so fast ($K_{PT} \sim 10^{10} \text{ sec}^{-1}$) that only acridinium type of emission is observed.

are present in the ground state we expect the ratio of acridinium and acridine emissions to be

$$\frac{I_{AH}}{I_A} = \frac{\epsilon_{AH}(\lambda_{ex}) \cdot C_{AH} \cdot \phi_{AH}}{\epsilon_A(\lambda_{ex}) \cdot C_A \cdot \phi_A}$$

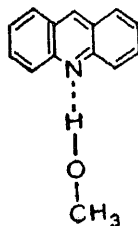
where (λ_{ex}) denote the extinction coefficient at the wavelength of excitation, C the concentration and ϕ_{ex} the quantum yield.

Substituting the numerical values at pH = 9 we obtain a theoretical value of 4×10^{-4} , whereas the actual observed value is 4×10^{-2} . Thus the presence of acridinium ions in the ground state is ruled out. An exciplex of acridine with OH^- also does not explain the red edge effect as in more alkaline solution the red edge emission diminishes. The structured emission may not be expected in an exciplex. Further, the effect is observed in frozen glass which cannot be due to the formation of exciplex. A ground state complex of acridine with OH^- is unlikely and is not observed in absorption or in excitation. As has already been mentioned, the non-alkaline solution shows a different type of red edge effect in as much as there is no change in the wavelength of emission but the structure of the bands improves. This sharpening of the structure is different from what has been observed in solid solutions or glasses due to heterogeneity of the emitting centres (Rudik and Pikulik 1971). However, in the solution state also we may assume various configurations of solute-solvent complexes and as suggested by Itoh and Azumi (1975) due to selective absorption at the red edge sharpening of the bands may result. However, the peculiarity about REE emission in alkaline solution at 295 K is that it resembles the low temperature acridinium emission in acidic solution. The REE emission at low temperature is also almost similar except that the room temperature REE emission is shifted to the red by a small amount $\sim 170 \text{ cm}^{-1}$. It is also interesting to note that the acridinium type REE emission itself shifts slightly on increasing the wavelength of excitation. This is apart from the subtle intensity changes which start appearing around 390 nm excitation. The temperature dependence of the reaction rate is an additional factor for our assumption of proton transfer in the excited state. Recent observations on proton reactions in the excited state have revealed that several types of hydrogen bonded complexes can occur in the excited state in the same solvent. They can be weakly or strongly hydrogen bonded, ion-pairs or completely protonated complexes. If it is assumed that K_{PT} is wavelength dependent at the red edge, many subtle changes occurring in the emission spectra can be qualitatively understood on this basis.

The protonation reactions in the excited state are generally diffusion controlled and/or there is proton tunnelling. While the diffusion-controlled reactions are viscosity dependent, the tunnelling rates are only temperature dependent. In any protonation reaction both the processes may be present simultaneously or exclusively any one may be present. The fact that the red edge effect is seen in frozen glass shows that the tunnelling effect is the predominant mode of proton transfer. Even the inconclusive isotope effect points towards the tunnelling effect. If it is assumed that the temperature dependence of the effect is indicated by an initiation

state proton transfer is unlikely considered. The proton may, however, involve a tunnelling process of proton transfer between the solvent oxygen atom and the nitrogen atom of the acridine.

The acridine molecule forms hydrogen bonded complexes, as shown below with solvent molecules—



The hydrogen bonded proton can occupy two positions—one near the oxygen of the alcohol and the other at nitrogen of acridine. In the latter case it behaves like a protonated molecule and/or an ion-pair complex. Due to the polarization of hydrogen bond by the nature of the medium and other factors many other stages may be possible. For our discussion we assume two potential minima for the proton in the excited state, the one with proton near N having a lower energy. According to Lowdin (1965) the rate constant for tunnelling of a particle of mass m through a double minimum potential barrier can be expressed as

$$K_{PT} = \nu \exp \left[\frac{-\pi^2 a_0 K}{h} (2 m V_0)^{1/2} \right],$$

where ν is the hit frequency, i.e., the number of times per second that the particle falls incident on the barrier, V_0 , a_0 are respectively the height and width of the potential barrier. K is the fraction of energy measured from the top of the barrier. At low temperatures most of the protons will be at the potential minimum while at higher temperatures there will be quite a large fraction of molecules in the higher energy region. Therefore at 80 K we may assume $K = 1$ and the rate of tunnelling becomes slower assuming that there are no other changes at low temperatures in the configurational diagram. We believe that the effect of OH⁻ ions on REE may also be due to changes in symmetries of the potential minima (Zundal 1976). This change may also account for the sharpening of the bands at room temperature because as the asymmetry increases the low frequency modes vanish. A tentative explanation for the change in proton transfer rate viscosity dependent, or based, on tunnelling can be had by suggesting that during the reaction process either promoting or non-promoting modes are active at REE. We suggest that after vibrational relaxation from the Franck-Condon state on SWE in a time $\sim 10^{-12}$ sec the excited molecule has enough time $\sim 10^{-9}$ sec to be equilibrated with the vibrationless excited S_1 state. If cage relaxation, orientational relaxation and other geometrical distortional relaxations are not completed within this time, a slight difference in energy may still be revealed in the wavelength shift of emission. This type of simple shift may be the same

SWE acridine type of emission is observed, which changes to acridinium type on REE near (0, 0) band. It is, thus, not a simple shift as is observed in some of the edge excitation red shift experiments reported by earlier workers. In recent years many photochemical reactions, quantum yields, lifetimes and other non-radiative processes (Avouris *et al* 1977 ; Rice 1974 ; Freed 1976) have been found to be dependent on the wavelength of excitation and certain broad features for these phenomena seem to be explicable on the basis of theories of non-radiative processes. However, the enormous difference in the proton transfer reactivity of the molecule relaxing to vibrationless excited singlet state and an energetically similar molecule prepared on absorption of the corresponding radiation frequency, is, however, not easily understood. Perhaps this situation is analogous to wavelength dependent non-radiative processes in aromatic molecules, e.g., the third channel in benzene (Jacon *et al* 1977).

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Micellar catalysed chlorination of acetophenone by chloramine-T

V RAGHUNATHAN, P S RAGHAVAN, K VAIDYANATHAN
and V S SRINIVASAN*

Department of Chemistry, Ramakrishna Mission, Vivekananda College,
Madras 600 004, India

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Abstract. The chlorination of acetophenone by chloramine-T CAT has been catalysed by anionic micelle, sodium lauryl sulphate (NaLS). Though the order in CAT is one, the order in acetophenone is fractional at lower concentration and becomes zero at higher concentration in the presence and absence of NaLS. This is probably due to the change in rate-determining step. At lower acetophenone concentration, the decomposition of enol-chlorinating species complex is rate-determining whereas at higher concentration, the formation of chlorinating species is rate determining. The graph of k_2 versus detergent concentration is sigmoidal and the positive co-operativity versus $\log[D]$ graph is 1.11, indicating possible interaction between micelle and substrate.

Keywords. Chlorination; acetophenone; anionic micelle; NaLS effect; positive co-operativity; chloramine-T.

1. Introduction

Chlorination of acetophenone using chloramine-T (CAT) has been investigated by Balasubramanian and Thiagarajan (1976) in HClO_4 medium and the reaction is an acid catalysed one. The present work is the result of our earlier finding that the surfactant, sodium laurylsulphate (NaLS), catalyses the chlorination of phenols (Rengarajan *et al* 1980) and amines (Raghavan *et al* 1980) by CAT. The present paper attempts to study the micellar influence on the chlorination of acetophenone by CAT.

The experiments have been so patterned such that the nature of the transition state and its stabilization in the micellar phase can be understood and a formal comparison can be attempted with enzyme catalysed reactions. Due to the limited solubility of acetophenone in water, all the reactions were carried out in 20% HOAc-80% H_2O (v/v) at 30° C.

2. Results and discussion

The kinetics of chlorination of acetophenone by CAT has been investigated in the binary solvent mixture of acetic acid-water in the presence of 0.20 M HClO_4 .

2.1 Dependence of rate on [CAT] and [Acetophenone]

The dependence of rate on [CAT] has been determined by varying the initial concentration of CAT at a given concentration of acetophenone, NaLS, HClO_4 and solvent composition. The disappearance of CAT follows first order kinetics both in the presence and absence of NaLS (table 1). The reaction rate depends on acetophenone concentration at lower levels. The order with respect to ketone is fractional but at a higher concentration of ketone, the reaction exhibits zero order kinetics (table 1). Similar trends have been observed in the chlorination of acetophenone (Balasubramanian and Thiagarajan 1976) and phenol (Balasubramanian and Thiagarajan 1975) by CAT.

2.2. Dependence of rate on detergent concentration

There is a gradual increase in rate with increasing concentration of anionic micelle, NaLS and this is marked above the initial micelle concentration 0.010 M (figure 1). This can be traced to a possible hydrophobic interaction of the phenyl ring with hydrocarbon core of the micelle while the side chain prefers the Stern layer of the micelle. The chlorinating species may be oriented such that the attack on the substrate becomes more facile. Similar catalysis by NaLS has been observed in the chlorination of anilines (Raghavan *et al* 1980) and phenols (Rengarajan *et al* 1980) by CAT.

Table 1. Dependence of rate on [CAT] and [Acetophenone].

$[\text{HClO}_4] = 0.20 \text{ M}$; $[\text{NaLS}] = 8.0 \times 10^{-3} \text{ M}$; 20% HOAc-80% H_2O (v/v) 30°C

[CAT] $\text{M} \times 10^3$	[Acetophenone] $\text{M} \times 10^3$	$k_1 \times 10^5 \text{ sec}^{-1}$
1.50	4.0	5.5
2.0	4.0	5.8
4.0	4.0	5.7
2.0	0.80	2.6
2.0	1.00	2.8
2.0	1.50	4.2
2.0	2.0	5.5
2.0	3.0	5.6
2.0	4.0	5.8
2.0	5.0	5.6

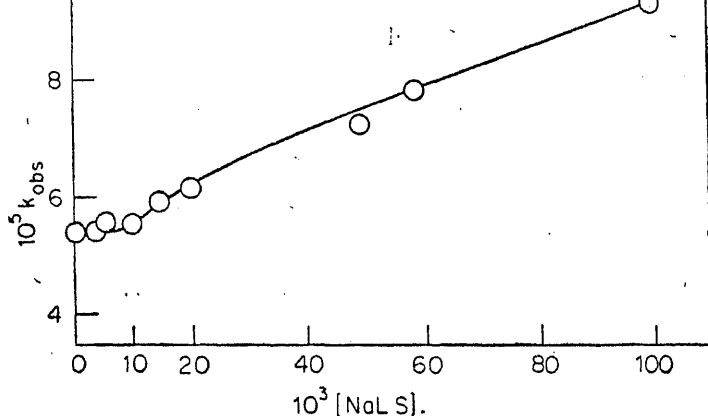


Figure 1. Dependence of rate on detergent concentration.

2.3 Temperature influence

The temperature influence over the reaction rate has been studied in the range of 30 and 50° C; and from the plots of $\log k_2$ versus $1/T$, the activation energies have been calculated. The enthalpies and entropies of activation thus evaluated are summarised in table 2.

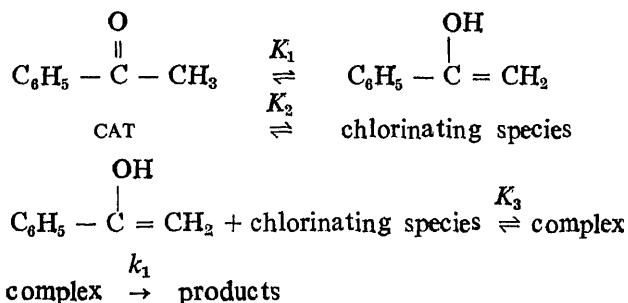
The lower activation energy observed in the micellar phase is in keeping with the rate enhancement noted in the presence of micelle.

2.4 Solvent influence

The rate of chlorination of acetophenone is affected by change in polarity of the solvent and the rate increases with increasing percentage of acetic acid (table 3).

3. Mechanism of chlorination of acetophenone in NaLS

As the order in acetophenone is fractional which then approaches zero at higher concentration, this reaction probably proceeds *via* the formation of a complex between the enol of acetophenone and CAT, exhibiting Michaelis-Menton type of kinetics. The above observations can be explained by the following reaction sequence;



where K and K_1 are composite of the constants K_1 , K_2 , K_3 and K_4 . At lower concentration of acetophenone, the decomposition of the complex seems to be rate-determining, exhibiting fractional order dependence on acetophenone. At higher concentration of acetophenone, the formation of active species from CAT seems to be rate-determining, exhibiting zero order dependence on ketone. It is further evidenced by the insensitivity of the rate to structural variation in acetophenone; both *p*-methyl and *p*-methoxy react with the rate comparable to the specific rate of chlorination of acetophenone itself at 0.040 M.

Table 2. Temperature dependence and thermodynamic parameters.

[Acetophenone] = 0.04 M; [CAT] = 0.002 M; [HClO₄] = 0.2 M; 20% HOAc-80% H₂O (v/v)

Temperature °C	(NaLS) M × 10 ³	$k_1 \times 10^3 \text{ sec}^{-1}$
30	..	4.5
30	8.0	5.8
40	..	11.8
40	8.0	12.2
50	..	25
50	8.0	29
	(a)	(b)
E_a kcal/mole	14.2	13.2
$\Delta H^\ddagger$ kcal/mole	13.6	12.6
$\Delta S^\ddagger$ kcal/mole	-0.033	-0.036

(a) in the absence of NaLS; (b) in the presence of NaLS.

Table 3. Dependence of rate on solvent composition.

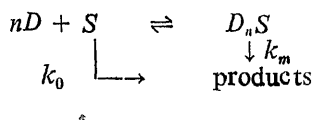
[Acetophenone] = 0.04 M; [CAT] = 0.002 M; [HClO₄] = 0.02 M; [NaLS] = 0.008 M;
Temp. 30° C.

Solvent composition %HOAc-%H ₂ O	$k_1 \times 10^3 \text{ sec}^{-1}$
20-80	5.8
30-70	7.1
40-60	8.5
50-50	12.0

4. Theoretical treatment of micellar catalysis

4.1. Positive co-operativity

On the basis of the mathematical model proposed by Bruice *et al* (1968)



where n is the number of detergent molecules (D), D_nS is catalytic micelle, K_D is the dissociation constant of micelle, k_m and k_0 are the rate constants in the micellar and aqueous phases respectively, the rate expression obtained is

$$\log \left[\frac{k_{\text{obs}} - k_0}{k_m - k_{\text{obs}}} \right] = n \log [D] - \log K_D.$$

From a graph of

$$\log \left[\frac{k_{\text{obs}} - k_0}{k_m - k_{\text{obs}}} \right] \text{ versus } \log [D], \text{ (figure 2) the slope, } n,$$

obtained is 1.11 which is considered as index of co-operativity (Piszkiewicz 1977). As the n value is greater than 1, it is referred to as positive co-operativity which implies the stimulation of the interaction of additional substrate molecules, by the interaction of the first molecule with micelle: K_D value obtained in this case is 2.1×10^{-2} M.

4.2. Binding model

By a scheme similar to the one considered above and taking into account the CMC of the detergents, the rate expression derived is,

$$k_{\text{obs}} = \frac{k_0 + k_m K [M]}{1 + K [M]} \text{ where}$$

$$[M] = \frac{C_D - \text{CMC}}{N},$$

C_D is the detergent concentration and N is the aggregation number of the detergent. From a graph of $1/(k_0 - k_{\text{obs}})$ against $1/(C_D - \text{CMC})$, the K/N value obtained is 15.8 M (figure 2).

5. Experimental

All liquid organic compounds were distilled using glass apparatus, rejecting head and tail fractions. HClO_4 (E Merck) was standardised, after dilution, against carbonate-free sodium hydroxide solution. NaLS is purified by washing with anhydrous ether and then recrystallising three to five times with 95% ethanol till

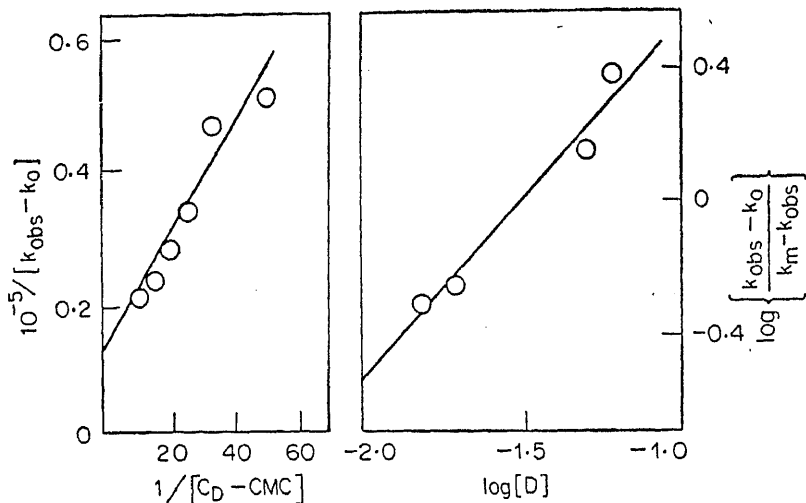


Figure 2. Plots for Piszkievicz and binding models.

The reaction rate has been followed by estimating unreacted CAT iodometrically at various intervals of time. The rate constants were evaluated by the numerical method using appropriate integrated rate expression. The specific rates are reproducible to within $\pm 4\%$. The stoichiometry of the acetophenone-CAT reaction is 1:1. The product of the reaction has been identified as phenacyl chloride by carrying out the analysis on a preparative scale.

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Reactions of indoles with mercury (II) salts

AVIJIT BANERJI* and MANJUSHA SARKAR (*née* CHAUDHURI)
Department of Pure Chemistry, University College of Science, Calcutta 700009,
India

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Abstract. A number of mercurated indoles were prepared. Their spectroscopic data (UV, IR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$) are reported. Our results contradict certain data appearing in previous reports on similar compounds. When heated in acetic acid mercurated compounds decomposed, although the products formed were not identical with those obtained earlier from the same substrates by the action of thallium(III) acetate in acetic acid. Reaction of 1-methylindole-3-mercuriacetate with styrene in the presence of lithium tetrachloropalladate furnished a product which was tentatively assigned the structure 9-methyl-1,3-diphenyl-1, 2, 3, 4-tetrahydrocarbazole.

Keywords. Indoles ; mercuration ; organomercurials.

1. Introduction

In the course of our work on the reactions of heterocycles with metal salts ; we investigated the reactions of indole and substituted indoles with thallium(III) acetate (Banerji and Ray 1978). A variety of oxidation products were obtained whose structures depended on the substituents at the 2- and 3-positions of indole. The results could be explained by assuming initial thallation of the indole to a 3-thallated indolenine, which reacted *in situ* to yield the products. In no case were we able to isolate the organo-thallium derivatives.

In contrast it was reported earlier (Mingoia 1930; Ramachandran and Witkop 1964; Yudin *et al* 1971) that mercury(II) salts react with indoles to give fairly stable isolable organo-mercuri derivatives. The complete characterisation of only a few of these has been described. Also, in the above-mentioned reports, there exists a great deal of confusion regarding the structures of these compounds as well as their spectroscopic data. Hence, we decided to re-investigate various aspects of the indole- HgX_2 ($\text{X} = -\text{OAc}$, $-\text{Cl}$) reaction with special reference to the spectroscopic properties of the products. The results of this investigation are reported in the present paper.

* To whom correspondence should be made.

media at room temperature (Ramachandran and Witkop 1964). The physical properties of the products obtained by using (i) one molar, (ii) two molar and (iii) excess of mercuric acetate, were very similar to those reported by Ramachandran and Witkop who characterised these as the "mono", "di-" and "tri-acetoxymercuri" derivatives respectively. The elemental analyses, however, showed that none of these products was pure. Products from (i) and (ii) contained less nitrogen than the formulation suggested by Ramachandran and Witkop. Hence it appears that mercuriation occurred to a greater extent than the "mono" and "di-acetoxymercuri" stage. It was not possible to accurately check mercuriation at these stages. As all the products were extremely insoluble in nature they could not be purified by crystallisation.

1-Methylindole-3-mercuriacetate (I), 1-methylindole-3-mercurichloride (II) and 1,3-dimethylindole-3-mercuriacetate (III) were obtained following the method of Yudin *et al* (1971) while 3-methylindole-2-mercuriacetate (IV) was also prepared by the method of Ramachandran and Witkop. These compounds could be obtained in pure state and gave the expected elemental (C, H, N) analyses.

The UV spectra of all the compounds were measured in ethanol and the data are given in table 1. Our results indicate that for compounds (I-IV) the absorption maxima suffered only a small but significant hypsochromic shift whereas the extinction coefficients were virtually unchanged. The mercury substituent has two vacant *p*-orbitals and exerts a -*R* conjugative effect on the aromatic nucleus which causes the observed hypsochromic shift in the UV spectra. Similar observations for phenyl-, thienyl- and furyl-mercury derivatives were noted earlier (Leandri and Tundo 1954). Ramachandran and Witkop (1964) had reported the UV spectral data of what they formulated as "mono-", "di-" and "tri-acetoxymercuri" indoles in about 2.5% acetic acid. These workers reported marked changes in the position of absorption maxima as well as very large enhancements in extinction coefficients when compared with the starting materials. Our results contradict these reports. The absorption maxima of the "mono-" ($\lambda_{\text{max}}^{\text{EtOH}}$ 218, 272, 277.5, 288 nm), and "di-acetoxymercuri" ($\lambda_{\text{max}}^{\text{EtOH}}$ 218, 272, 277.5, 288 nm) compounds showed the same small hypsochromic shift compared to indole ($\lambda_{\text{max}}^{\text{EtOH}}$ 216, 266, 276, 287 nm) as observed for the other compounds. Moreover, no perceptible shifts of the absorption maxima of these two compounds, or in fact of any of the other mercurated products, were observed when the medium was changed from ethanol to 2.5% acetic acid. The extinction coefficients for the two products obtained from indole calculated on the basis of mono- and di-acetoxymercuriation are considerably less than those expected. This is in conformity with the elemental analyses which showed the occurrence of mercuriation beyond the desired stage.

We report here the IR spectra of the mercurated indoles for the first time. The important bands and their assignments are listed in table 2. The spectra were recorded in Nujol mull using polyethylene discs. The C-Hg stretching bands appeared at 400-415 cm^{-1} for all the compounds. When the IR spectra were recorded in KBr pellets, additional bands appeared at 335-340 and 505-550 cm^{-1}

IR spectrum of 1,3-dimethyl-2-acetoxymmercuri-indole is given in figure 1, with the more important assignments. The different impure mercurated products ("mono-", "di-" and "tri-acetoxymmercuri") from indole also showed C-Hg stretching at 400-415 cm^{-1} .

NMR investigation of mercuri-indole was also carried out (table 3). Some ^1H -NMR data had been earlier reported by Ramachandran and Witkop (1964) using trifluoroacetic acid (TFA) as the solvent. They made certain structural assignments on the basis of these observations; in particular the "di-acetoxymmercuri" derivative was assigned the structure 2,3-diacetoxymmercuri-indole. It seems that no reliance can be placed on these data for the following reasons: Firstly in TFA medium the indoles will certainly exist as 3-protonated indolenine species rather than free species; Secondly in the strong acid medium used demercuration would easily occur so that the reported values may not refer to the mercurated compounds at all.

We found that for the 1-methyl-3-acetoxymmercuri-indole, the C-2 proton and N-methyl group were slightly de-shielded with respect to 1-methyl indole. There were also changes in the signals for the benzenoid protons. In the parent heterocycle all these protons appeared as a complex multiplet centred around δ 7.2, whereas in the mercuri-derivative one of these moved downfield to appear as a double doublet at δ 7.50 ($J_a = 6.1$ Hz, $J_m = 1.5$ Hz). This signal was presumably due to the C-4 proton, which is shielded by the 3-acetoxymmercuri grouping.

The 20 MHz ^{13}C -NMR of 1-methyl-3-acetoxymmercuri-indole was recorded in DMSO- d_6 . Tentative assignments based on single-frequency off-resonance decoupling (SFORD) multiplicities and chemical-shift theory are given in figure 2. ^{13}C -NMR spectra of the other compounds could not be recorded on account of their poor solubility in the more common deuterated solvents.

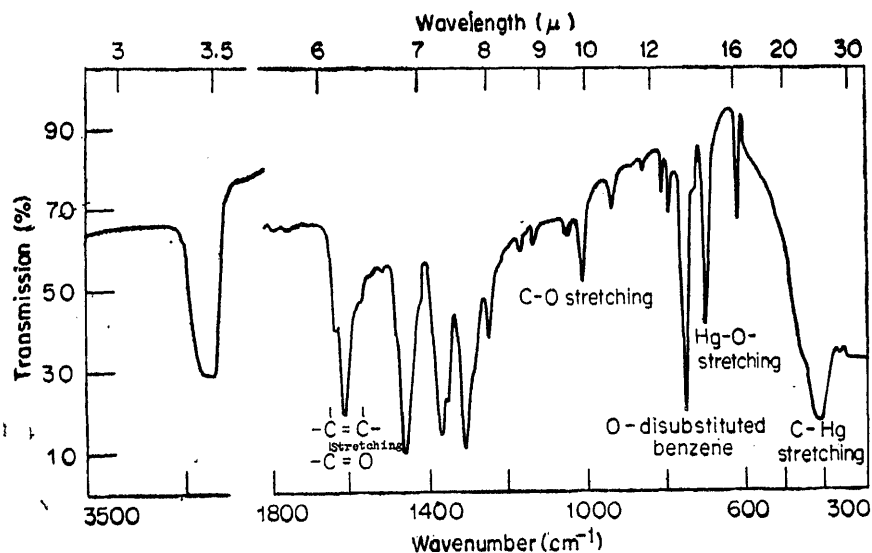


Figure 1. IR spectrum of 1,3-dimethyl-2-acetoxymmercuri-indole recorded in the Perkin-Elmer 620 cm^{-1} was recorded at higher

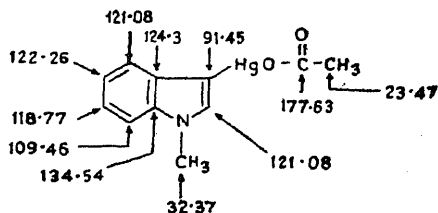


Figure 2. 20 MHz ^{13}C NMR Spectral data (CDCl_3) (in ppm) of 1-methyl-3-acetoxy mercuri-indole.

Table 1. uv absorption maxima of mercurated indoles (in 95% ethanol),

Compound (in EtOH)	λ_{max} (log ϵ) in nm
2-Acetoxymercuri-skatole	226 (4.32), 290 (3.90), 296 (3.90)
Skatole*	222 (4.50), 275 (3.73), 282 (3.78), 2.90 (3.69)
1-Methyl-3-acetoxymercuri-indole	222 (4.58), 272.5 (3.90), 284 (3.89), 295 (3.80)
1-Methylindole-3-mercuri-chloride	222 (4.58), 270 (sh) (3.76), 283 (3.77), 295 (3.67)
1-Methylindole*	219 (4.54), 275 (3.77), 282 (3.78), 293 (3.66)
1,3-Dimethyl-2-acetoxy-mercuri-indole	228 (4.43), 292.5 (3.99)
1,3-Dimethyl-indole*	225 (4.50), 248 (3.72), 278 (3.68)
Indole*	216 (4.54), 266 (3.76), 276 (3.76), 287 (3.68)

* Houlihan (1972).

Table 2. IR absorption bands of mercurated indoles (in nujol mull recorded in polythene discs).

Compound	ν (in cm^{-1})				
	Acetate*		o-Disubstituted benzene	Hg-O	Hg-C
	$>\text{C}=\text{O}$	$-\text{O}-\text{C}-$ stretching			
2-Acetoxymercuri-skatole	1580	1010	725	680	405
1-Methyl-3-acetoxymercuri-indole	1600	1005	730	690	400
1,3-Dimethyl-2-acetoxy-mercuri-indole	1600	1010	750	700	415
1-Methylindole-3-mercuri-chloride	...	...	750	...	410

* Structure of acetate ion: CH_3COO^- . Source: Houlihan (1972).

Table 3. 80 MHz ^1H -NMR spectral data of mercurated indoles.

Compound	Signal at δ (ppm)			
	Solvent	$-\text{OCOCH}_3$	Aromatic protons	Other protons
Mono-acetoxy-mercuri-skatole	DMSO- d_6	1.87	6.70-7.80	$-\text{CH}_3$ merged with DMSO peak
1-Methylindole-3-mercuri-acetate	CDCl_3	2.05 (3H, s)	6.95 (1H, br, s) 7.08-7.30 (3H, m) 7.50 (1H, dd, $J_o = 6.1$ Hz, $J_m = 1.5$ Hz)	$-\text{N}-\text{CH}_3$ 3.76 (3H, s)
1,3-Dimethylindole-2-mercuri-acetate	CDCl_3	2.01 (3H, s)	6.94-7.37 (4H, m)	$-\text{N}-\text{CH}_3$ 3.37 (3H, s) $\text{C}-\text{CH}_3$ 2.21 (3H, s)
1-Methylindole-3-mercuri-chloride	DMSO- d_6		6.94-7.30 (3H, m); 7.38 (1H, dd, $J_o = 8.8$ Hz, $J_m = 1.8$ Hz; 7.65 (1H, dd, $J_o = 7.7$ Hz, $J_m = 2.6$ Hz)	$-\text{N}-\text{CH}_3$ 3.74 (3H, s)

As mentioned earlier, the reaction of indoles with TTA in acetic acid gave oxidation products. It was of interest to find out whether the mercuri-indoles would also be converted to similar products under similar or more vigorous reaction conditions. It was found that the mercurated compounds remained largely unaffected when subjected to reaction conditions similar to those used for the TTA reaction. When more vigorous conditions were used, none of the products previously obtained with TTA was formed though some, demercuration to the original compounds occurred. Most of the material underwent decomposition to intractable products. In the case of mono-acetoxymercuri-indole, oxindole was formed in low yield on heating with glacial acetic acid for 4 hours.

2.1. Reaction of 1-methylindole-3-mercuri-acetate with styrene

The palladium salt-catalysed olefin arylation reaction provides a very convenient route to a wide variety of olefinic compounds (Heck 1968). We attempted the

of unstable products were formed, of which only one of the major compounds could be isolated in a reasonably pure state by preparative TLC. None of the others could be isolated by TLC as they underwent decomposition. The isolated product, which exhibited a typical indolic UV spectrum ($\lambda_{\text{max}}^{\text{EtOH}}$ 225, 277-278 (sh) nm), was tentatively assigned the structure 9-methyl-1,3-diphenyl-1,2,3,4-tetrahydrocarbazole (3) primarily on the basis of its ^1H -NMR spectrum. A variety of possibilities exist for alternative combinations with styrene, of which only that shown was compatible with the ^1H -NMR (see experimental for chemical shifts) (figure 3).

The formation of the product (3) can be mechanistically rationalised as shown in scheme 1.

3. Experimental

All melting points are uncorrected and were determined on an electrically heated Koffler Block melting point apparatus. The UV spectra were measured on a Varian 634S spectrophotometer in 95% aldehyde free ethanol. The IR spectra were

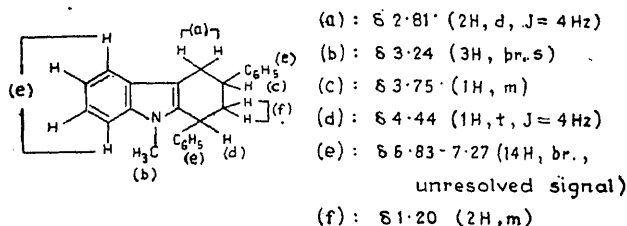
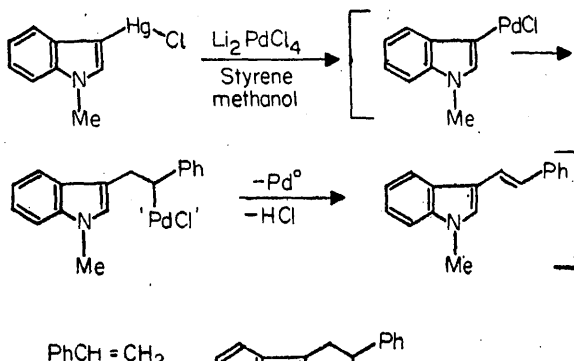


Figure 3. 80MHz ^1H -NMR spectral data of 9-methyl-1,3-diphenyl-1,2,3,4-tetrahydrocarbazole.

Scheme-1



recorded in polythene disc on a Beckman IR-20 spectrophotometer. The ^1H - and ^{13}C -NMR spectra were recorded on Varian Associates CFT-20 NMR spectrometer.

3.1. 2-Acetoxymercuri-skatole

Mercuric acetate (1.59 g, 5 mmol) in absolute ethanol (15 ml) was added in portions to a magnetically stirred solution of skatole (0.66 g, 5 mmol) in absolute ethanol (10 ml) whereby a pale yellow dispersion was formed. The mixture was stirred for 2 hr and left overnight. The pale yellow precipitate was filtered and washed thoroughly with absolute ethanol (yield 1.1 g, 57.9%); m.p. 180° (d). Found C 35.5%, H 3.1%, N 3.6%; $\text{C}_{11}\text{H}_{11}\text{O}_2\text{NHg}$ requires C 35.7%, H 3.2%, N 3.6%.

3.2. 1-Methyl-3-acetoxymercuri-indole and 1,3-dimethyl-3-acetoxymercuri-indole

1-Methylindole and 1,3-dimethylindole were prepared according to Heaney and Steven (1973).

To a stirred solution of the methylated indole (5 mmol) in absolute ethanol (10 ml), mercuric acetate (1.59 g, 5 mmol) in absolute ethanol (15 ml) was added and left overnight. The white precipitate was filtered off, washed and dried.

3.2a. 1-Methyl-3-acetoxymercuri-indole. Yield 1.7 g, 89.4%; m.p. 187° (d). Found C 34.2%, H 2.2%, N 3.5%; $\text{C}_{11}\text{H}_{11}\text{O}_2\text{NHg}$ requires C 33.9%, H 2.3%, N 3.6%.

3.2b. 1,3-Dimethyl-3-acetoxymercuri-indole. Yield 1.1 g, 55.0%; m.p. $144-6^\circ$. Found C 35.6%, H 3.2%, N 3.7%; $\text{C}_{12}\text{H}_{13}\text{O}_2\text{NHg}$ requires C 35.7%, H 3.2%, N 3.4%.

3.3. 1-Methylindole-3-mercurichloride

1-Methylindole (0.66 g, 5 mmol) and sodium acetate (1.6 g, 20 mmol) were dissolved in anhydrous methanol (10 ml), and mercuric chloride (1.36 g, 5 mmol) in methanol (15 ml) was added. A white precipitate appeared instantaneously, which was filtered, washed and dried (yield 1.5 g, 83.3%), m.p. 170° (d) (Yudin *et al* 1971, $170-3^\circ$). Found C 35.6%, H 1.9%, N 3.7%; $\text{C}_9\text{H}_8\text{ClNHg}$ requires C 35.6%; H, 1.9%, N 3.8%.

3.4. Reaction of 1-methylindole-3-mercuriacetate and styrene in presence of Li_2PdCl_4

To a mixture of 1-methylindole-3-mercuriacetate (0.97 g, 2.5 mmol) and styrene (0.6 ml, > 5 mmol); 0.1 (M) Li_2PdCl_4 (50 ml, 5 mmol) in methanol was added dropwise over a period of 1 hr and then stirred for 48 hr in an atmosphere of nitrogen. The mixture was filtered, the solvent removed and the residue was extracted with methylene chloride. The residue from the methylene chloride extract was purified by column chromatography and PTLC. 9-methyl-1,3-diphenyl-

80 MHz NMR spectral data of (3) (in $CDCl_3$): (a) δ 2.81 (2H, d, $J = 4$ Hz); (b) δ 3.24 (3H, broad s); (c) δ 3.75 (1H, m); (d) δ 4.44 (1H, t, $J = 4$ Hz); (e) δ 6.83–7.27 (4H, broad unresolved signal), (f) δ 1.20 (2H, m).

3.5. Mono-acetoxymercuri-indole

To a stirred solution of indole (0.59 g, 5 mmol) in absolute ethanol (10 ml); mercuric acetate (1.59 g, 5 mmol) in absolute ethanol (15 ml) was added portion-wise. The reaction mixture was allowed to stand overnight, filtered, the residue washed with ethanol and dried (yield 1.2 g, 66.6% on basis of mono-mercuration); m.p. 266° (d) [Ramachandran and Witkop 1964, 270° (d)]. Found N 2.2%, $C_{10}H_9O_2NHg$ requires N 3.7%.

3.6. Di-acetoxymercuri-indole

Di-acetoxymercuri indole was prepared similarly using two moles of mercuric acetate (3.17 g, 10 mmol). The product was isolated in a similar manner (yield 2.7 g, 98.1% on basis of di-mercuration); m.p. 205° (d) [Ramachandran and Witkop 1964, 205° (d)]. Found N 1.9%; $C_{12}H_{11}O_4NHg_2$ requires N 2.2%.

3.7. Tri-acetoxyme-curi-indole

Indole was mercurated with excess of mercuric acetate (6.36 g, 20 mmol) following the same procedure. A precipitate rapidly formed and then redissolved. The alcohol was removed under reduced pressure. The residue was triturated with water, filtered and then washed successively with water, ethanol and ether (yield 0.5 g, 10.7% on basis of tri-mercuration); m.p. 268–9° (d) [Ramachandran and Witkop 1964, 270° (d)]. Found N 1.8%, $C_{14}H_{13}O_6NHg_3$ requires N 1.6%.

Acknowledgement

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Quantitative structure activity relationships—Part V. Release and uptake of norepinephrine in murine heart by phenethylamines

VIJAY GOMBAR

Department of Pharmaceutical Sciences, Panjab University, Chandigarh 160 014, India.

MS received 24 September 1981

Abstract. Quantitative structure activity studies have been carried out on a series of hydroxyphenethylamines. The calculated Fujita-Ban group contributions indicate that the *m* and *p*-hydroxyphenethylamines have high affinity for uptake and efflux of radioactive norepinephrine. The highly negative contribution of the —OH group at the second ortho position indicates that the derivatives with hydroxyl groups at both the ortho positions should have no activity or extremely low activity as inhibitors of uptake and as releasing agents.

Keywords. Fujita-Ban calculations ; norepinephrine ; phenethylamines.

1. Introduction

The *in vivo* effects of various compounds on uptake and release of radioactive norepinephrine have been studied in detail. The results of a series of investigations by Axelrod *et al* (1961, 1962), Hertting *et al* (1961, 1962), Daly *et al* (1966) and Creveling *et al* (1966, 1967, 1968, 1974) include structure-activity relationships concerning inhibition of norepinephrine uptake at plasma membrane and its displacement from the storage sites. The different behaviours of ortho-hydroxyphenethylamines and ortho-hydroxyphenethanolamines towards inhibition of uptake of radioactive norepinephrine (Rotman *et al* 1975) provide some insight into the structural requirements of uptake sites.

The present paper embodies quantitative structure-activity studies concerning the effects of hydroxyl groups from various positions in phenethylamine on *in vivo* inhibition of uptake of [³H] norepinephrine into, and its release from, murine heart.

2. Method and data set

For phenethylamine(I) and its hydroxy derivatives Rotman *et al* (1975) have assayed inhibition of uptake and release of radioactive norepinephrine by measurement of

Part I ; Singh *et al* (1980), Part II ; Gombard *et al* (1981), Part III ; Jain and Gombard (1981), Part IV ; Gombard and Wadhwa (1982).

the amount of [^3H]-DL-norepinephrine. Both these activities have been expressed in terms of ED_{50} (mol/kg).

In the present work the observed activity, however, refers to $-\log \text{ED}_{50}$ where ED_{50} is taken in mol/kg units. The present quantitative structure-activity studies are carried out in the light of the Fujita-Ban *de novo* model (Fujita and Ban 1971) because the purpose of this study is to quantify the effect of hydroxyl group at different positions in the aromatic ring of phenethylamine. The group contributions have been calculated as per Kubinyi's algorithm of converting the Fujita-Ban matrix into normal equations matrix followed by simultaneous equations' solution by any of the standard methods (Kubinyi 1977). A computer program FUJKUB, fully incorporating this algorithm was developed by the author and used for the present work. All data were processed on the DECSYSTEM-2050 at the Regional Computer Centre (North), Chandigarh, India.

3. Results

The structures, observed activities and Fujita-Ban matrix for phenethylamines exhibiting inhibition for uptake of norepinephrine are given in table 1. This information about phenethylamines eliciting release of norepinephrine is collected in in table 2. Both these sample sets are statistically unbiased as the observed activity is found to vary about two log units which corresponds to 100-fold difference in activity. Tables 3 and 4 respectively contain the normal equations matrices corresponding to the Fujita-Ban matrices in tables 1 and 2. In tables 3 and 4 μ_0 represents contribution by the unsubstituted arbitrary reference (phenethylamine) and λ_x represents the contribution by the group X. The group contributions calculated in the two cases (figure 1) lead to the following correlations.

$$\begin{aligned}
 -\log \text{ED}_{50} (\text{uptake}) &= 5.80 - 0.40 [2\text{-OH}] + 0.36 [3\text{-OH}] \\
 &\quad + 0.27 [4\text{-OH}] + 0.003 [5\text{-OH}] - 1.10 [6\text{-OH}] \\
 n &= 15 ; r = 0.806 ; s = 0.416
 \end{aligned} \tag{1}$$

$$\begin{aligned}
 -\log \text{ED}_{50} (\text{release}) &= 3.87 - 0.39 [2\text{-OH}] + 0.36 [3\text{-OH}] \\
 &\quad + 0.50 [4\text{-OH}] + 0.42 [5\text{-OH}] \\
 n &= 14 ; r = 0.755 ; s = 0.468
 \end{aligned} \tag{2}$$

It is observed that these correlations are significant almost at 95% level.

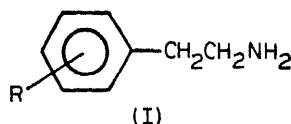
4. Discussion

4.1. Inhibition of uptake of norepinephrine

It is evident from the contributions of hydroxyl group at different positions (figure 1a) that phenethylamines with -OH substituent at *m* or/and *p*-positions

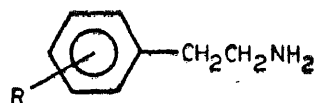
have relatively high affinity as *in vivo* inhibitors of the uptake of norepinephrine. It is obvious from the minus sign of the group contribution of 2-OH that the presence of an orthohydroxy group in phenethylamine would reduce the inhibition affinity. In (I) the negative sign and fairly high magnitude of the contribution by 6-OH group further reveals that phenethylamines with hydroxy groups occupying both the ortho positions must be extremely weak inhibitors. This is in accord with the results reported by Rotman *et al* (1975). In most of the phenethylamines bearing two ortho hydroxy groups they did not observe any inhibition even for concentrations as high as 100 $\mu\text{mol/kg}$.

Table 1. Structures, Fujita-Ban matrix and activity of phenethylamines investigated for *in vivo* inhibition of $^3\text{[H]}$ norepinephrine uptake into murine heart.



Compound No.	R	Independent substituents					Activity	
		2-OH	3-OH	4-OH	5-OH	6-OH	Obsd.	Calcd.
1	H						5.42	5.80
2	2-OH	1					4.86	5.40
3	3-OH		1				6.46	6.16
4	4-OH			1			6.16	6.07
5	2,3-(OH) ₂	1	1				5.93	5.76
6	2,4-(OH) ₂	1		1			5.77	5.66
7	2,5-(OH) ₂	1			1		5.63	5.40
8	3,4-(OH) ₂		1	1			6.49	6.43
9	3,5-(OH) ₂		1		1		6.21	6.17
10	2,3,4-(OH) ₃	1	1	1			6.20	6.03
11	2,3,5-(OH) ₃	1	1		1		5.92	5.76
12	2,3,6-(OH) ₃	1	1			1	4.66	4.66
13	2,4,5-(OH) ₃	1		1	1		6.14	5.66
14	3,4,5-(OH) ₃		1	1	1		6.31	6.43

Table 2. Structures, Fujita-Ban matrix and activity of phenethylamines investigated for *in vivo* release of [³H] norepinephrine from murine heart.



Compound No.	R	Li dependent substituents				Activity	
		2-OH	3-OH	4-OH	5-OH	Obsd.	Calcd.
1	H					3.29	3.87
2	2-OH	1				3.22	3.47
3	3-OH		1			4.64	4.23
4	4-OH			1		4.42	4.37
5	2,3-(OH) ₂	1	1			4.23	3.83
6	2,4-(OH) ₂	1		1		4.19	3.97
7	2,5-(OH) ₂	1			1	3.70	3.89
8	3,4-(OH) ₂		1	1		4.72	4.73
9	3,5-(OH) ₂		1		1	4.94	4.65
10	2,3,4-(OH) ₃	1	1	1		4.13	4.33
11	2,3,5-(OH) ₃	1	1		1	4.20	4.25
12	2,4,5-(OH) ₃	1		1	1	5.15	4.39
13	3,4,5-(OH) ₃		1	1	1	5.00	5.15
14	2,3,4,5-(OH) ₄	1	1	1	1	4.10	4.75

Table 3. Normal equations matrix for norepinephrine uptake inhibition studies.

15	9	9	7	6	1	μ_0	87.39
9	9	5	4	4	1	λ_{2-OH}	50.35
9	5	9	4	4	1	λ_{3-OH}	53.43
7	4	4	7	3	0	λ_{4-OH}	42.31
6	4	4	3	6	0	λ_{5-OH}	35.45
1	1	1	0	0	1	λ_{6-OH}	4.66

Table 4. Normal equations matrix for norepinephrine release studies.

14	8	8	7	6	μ_0		59.92
8	8	4	4	4	λ_{2-OH}		32.91
8	4	8	4	4	λ_{3-OH}	=	35.95
7	4	4	7	3	λ_{4-OH}		31.71
6	4	4	3	6	λ_{5-OH}		27.09

* See table 3.

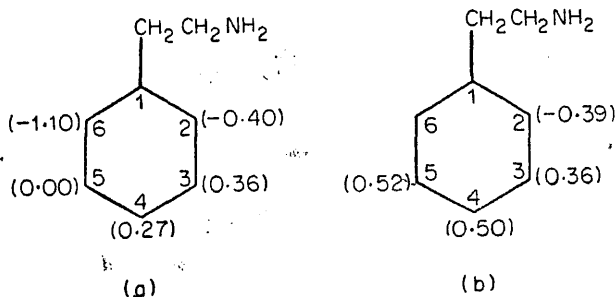


Figure 1. Fujita-Ban group contribution of -OH group at different positions in phenethylamine as a. inhibitors of uptake, b. releasers of norepinephrine.

4.2. Release of norepinephrine

The pre-requisite for release of norepinephrine is its active uptake into the neuronal terminal though transport of amine into the cell after binding to the uptake site is an important factor. Therefore, the compounds with poor affinity for uptake are expected to be poor releasers of norepinephrine as well. This is quite evident from (2). The contribution of 2-OH group is once again negative (figure 1b). This amounts to say that phenethylamines with -OH group at ortho position are poor releasing agents. These phenethylamines have already been shown to have poor affinity for uptake (§ 4.1). It can be further seen that 2,3,6-trihydroxyphenethylamine which has both the ortho positions occupied by -OH groups, has extremely low affinity for uptake and should be expected to be a still poorer releasing agent. Indeed, this compound does not figure in table 2 as Rotman *et al* (1975) observed that ED_{50} for this compound was very high

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Magnetic susceptibility studies of $\text{Mn}_{1-x}\text{M}_x\text{O}$ ($M = \text{Zn}, \text{Mg}, \text{Fe}$)

C E DESHPANDE, P P BAKARE, M N S MURTHY,
N Y VASANTHACHARYA* and P GANGULY*

National Chemical Laboratory, Pune 411 008, India

*Solid State and Structural Chemistry Unit, Indian Institute of Science,
Bangalore 560 012, India

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Abstract. Magnetic susceptibility studies of $\text{Mn}_{1-x}\text{M}_x\text{O}$ ($M = \text{Zn}$, $x \leq 0.1$; $M = \text{Mg}$, $x \leq 0.12$; $M = \text{Fe}$, $x \leq 0.4$) in the range 77 to 300 K are reported. The methods of preparation of $\text{Mn}_{1-x}\text{M}_x\text{O}$ systems preclude the presence of trivalent ions. The $\text{Mn}_{1-x}\text{Fe}_x\text{O}$ system shows anomalous behaviour around $x = 0.2 - 0.3$. The results are discussed in terms of competition between the nearest neighbour and the next-near-neighbour interactions, dilution effects and cooperative effects of FeO_6 octahedra.

Keywords. MnO ; FeO ; magnetic susceptibility.

1. Introduction

Magnetic susceptibility of MnO and its solid solutions with other ions such as Mg , Zn and Fe have been extensively studied by several workers (Millar 1928; Foex 1948; Seino *et al* 1973; Jagadeesh and Seera 1980; Evrard 1971; Hope *et al*). Hope *et al* have investigated the system $(\text{Mn}_{1-y}\text{Fe}_y)_x\text{O}$ ($y < 1.0$) which always has a slight excess of oxygen. Murthy and coworkers (Deshapande and Murthy 1981; Deshapande *et al* 1978) have recently reported the preparation of MnO stabilized by small amounts of Zn and also $\text{Mn}_{1-x}\text{Fe}_x\text{O}$ ($x < 0.4$) which are very resistant to oxidation. Thus, the $\text{Mn}_{1-x}\text{Fe}_x\text{O}$ system has no excess oxygen for $x < 0.4$. In this paper, we report the results of our studies of the magnetic susceptibilities of $\text{Mn}_{1-x}\text{M}_x\text{O}$ ($M = \text{Mg}, \text{Fe}$ and Zn) in the 77-300 K range.

2. Experimental

The $\text{Mn}_{1-x}\text{M}_x\text{O}$ systems were prepared according to the procedure of Murthy and coworkers (Deshapande and Murthy 1981; Deshapande *et al* 1978). X-ray lattice parameters were determined using a Phillips PW 1050 diffractometer.

measured using $\text{HgCo}(\text{SCN})_4$ for calibration purposes. The field used was 3000 gauss.

3. Results and discussion

3.1. X-ray diffraction studies

Crystal structures of these solid solutions are all of the rocksalt type. The cubic unit cell parameters of these solid solutions are given in table 1. All the samples show a linear decrease in the unit cell dimensions with increasing x as expected of Vegard's law behaviour (figure 1).

3.2. Magnetic susceptibility studies

Magnetic susceptibility studies of these compounds were carried out below 300 K. All the samples showed a maximum in the susceptibility at a temperature T_{max} which could be associated with the antiferromagnetic ordering temperature T_N . The χ_M^{-1} vs T plots of these compounds are shown in figures 2-4. The magnetic susceptibility of the $\text{Mn}_{1-x}\text{Zn}_x\text{O}$ and $\text{Mn}_{1-x}\text{Mg}_x\text{O}$ samples were normalised for one g atom of Mn. Such a normalisation was not carried out for the $\text{Mn}_{1-x}\text{Fe}_x\text{O}$ compounds. The values of μ_{eff} and θ calculated from the slopes of these lines above 200 K from a least squares fit are given in table 1. Because of the broad

Table 1. X-ray parameters and magnetic properties of $\text{Mn}_{1-x}\text{M}_x\text{O}$ compounds.

Compound	x	a , Å (± 0.003)	μ_{eff} B	θ (K)	T_{max} (K)
$\text{Mn}_{1-x}\text{Zn}_x\text{O}$	0.001	4.449	5.63	533	127
	0.005	..	5.77	568	125
	0.010	..	5.98	629	123
	0.050	4.443	6.14	667	119
$\text{Mn}_{1-x}\text{Mg}_x\text{O}$	0.001	4.450	5.82	573	120
	0.005	4.451	5.72	547	119
	0.010	4.449	5.73	568	118
	0.050	4.439	5.44	460	116
	0.10	4.430	5.44	440	114
	0.12	4.426	5.47	435	110
	0.15	4.419	5.45	445	100
$\text{Mn}_{1-x}\text{Fe}_x\text{O}$	0.1	4.435	5.27	358	126
	0.2	4.425	4.94	210	138
	0.3	4.412	5.20	238	130

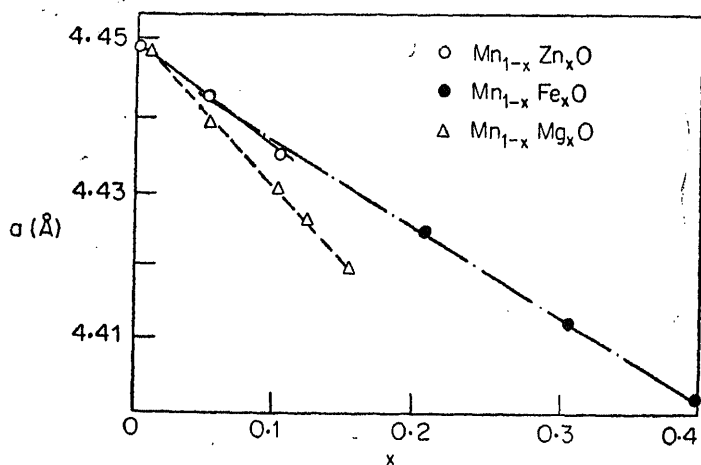
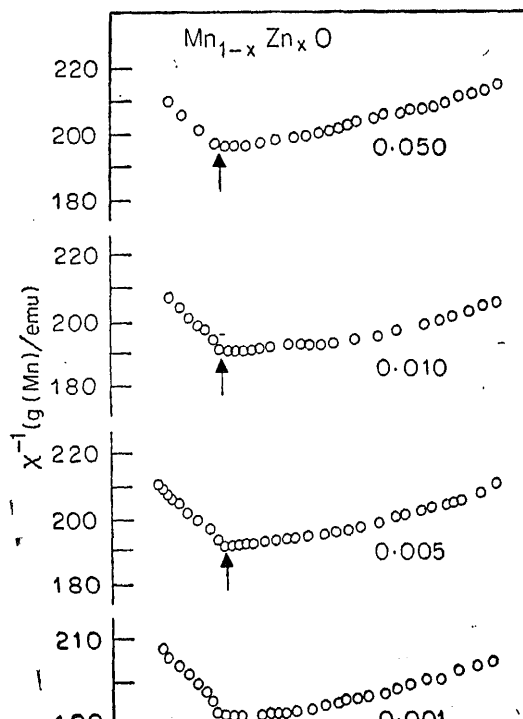


Figure 1. Variation of unit cell parameter with increasing x for the $Mn_{1-x}M_xO$ system.



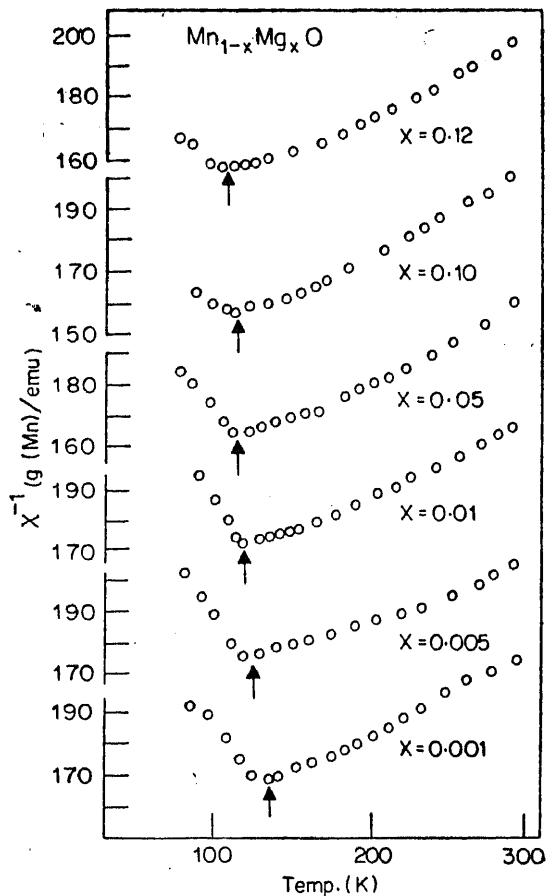
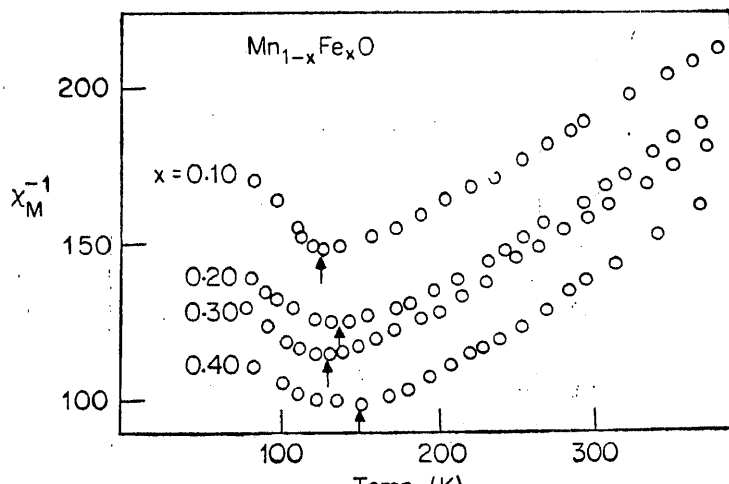


Figure 3. χ^{-1} vs T plots of $\text{Mn}_{1-x}\text{Mg}_x\text{O}$.



the true high temperature values. The trends are, however, likely to be real.

MnO exhibits a broad susceptibility maximum which is slightly above the ordering temperature T_N ; T_N itself is characterized by a sharp inflection point in the susceptibility. In the rock-salt structure both the nearest neighbour cation-cation interaction J_{nn} and the next-near-neighbour cation-anion-cation interaction J_{nna} are possible. In 3d transition metal monoxides, J_{nna} is the dominant interaction and this leads to magnetic ordering of the second kind in the fcc structure (Goodenough 1963). The broad maximum in the susceptibility is probably due to competing interactions and frustrations inherent in the rock-salt structure which cannot sustain a magnetic order in which all interactions are antiferromagnetic. At T_N rhombohedral distortion takes place which reduces the unit cell length thus strengthening antiferromagnetic interactions and weakening ferromagnetic interactions between nearest neighbours. This exchange striction which is a cooperative process is likely to be damped strongly in the presence of non-magnetic impurities.

3.3. $Mn_{1-x}Mg_xO$ and $Mn_{1-x}Zn_xO$

In these compounds the sharpness of the inflection point decreases with increasing Mg or Zn concentration (figures 2 and 3). The maxima broaden considerably and T_{max} shifts to lower temperatures with increasing x . The substitution of Zn or Mg for Mn probably affects the cooperative nature of the exchange striction process so that long-range ordering is affected. The magnetic structure is broken into clusters with short-range interactions. This is the usual dilution effect.

3.4. $Mn_{1-x}Fe_xO$

Substitution of Fe for Mn leads to a decrease in θ . In FeO, $\theta/T_N \sim 1$ which is indicative of a $J_{nn} = 0$ whereas a $\theta/T_N \sim 5$ in MnO is indicative of $J_{nn} \neq 0$. The θ and μ_{eff} values of these solid solutions are given in table 1. The θ values and T_N ($\sim T_{max}$) are in reasonably good agreement with earlier results (Evrard 1971; Hope *et al*). There is however an anomaly around $x = 0.3$ with respect to the T_{max} and θ (table 1). This sample also shows a broad minimum in the inverse susceptibility curve (figure 4). The anomalous behaviour could be representative of the solid solutions $Mn_{1-x}Fe_xO$ as distinct from the $(Mn_{1-x}Fe_xO)_yO$ ($y < 1$) studied by earlier workers (Evrard 1961; Hope *et al*). A Mössbauer study of our samples has shown the absence of Fe^{3+} ions. The broad nature of the susceptibility around T_N for the $x = 0.3$ samples seem to show the presence of iron-rich and Mn-rich clusters. Hope *et al* have reported the results of the quadrupole splitting, ΔE_Q , at the Fe nucleus in $(Fe_{1-x}Mn_x)_yO$ systems. Their results show that for small values of x , ΔE_Q is small reflecting essentially the symmetrical environment of MnO_6 octahedra. With increasing x , ΔE_Q increases rapidly showing the formation of distorted FeO_6 octahedra. There seems to be some evidence of a change in the slope of the ΔE_Q vs x plot around $x = 0.2-0.3$ and the ΔE_Q values are very close to the value found in 'FeO' in this range.

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Liquid structure of vanadium tetrachloride from neutron diffraction study

R V GOPALA RAO* and B M SATPATHY

Physical Chemistry Section, Jadavpur University, Calcutta 700 032, India

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Abstract. Assuming the separation of the intermolecular scattering function into the radial and angular parts and using Egelstaff *et al*'s orientational model for tetrachlorides, the structure of liquid vanadium tetrachloride has been studied. It has been observed that such a separation is approximate for this liquid and the introduction of a third correction term is required to account for the molecular structure function. The chlorine-chlorine partial structure and effective angle-averaged intermolecular chlorine-chlorine potential in the liquid has been evaluated. Without taking the third correction term, introduced to generate theoretically the molecular structure function, the centre structure function has been obtained in an approximate way from the experimentally observed molecular structure function and from it the centre radial distribution function, centre direct correlation function and the angle-averaged vanadium-vanadium effective potential has been evaluated.

Keywords. Liquid structure ; vanadium tetrachloride ; intramolecular function ; intermolecular scattering function ; orientational correlation ; partial structure.

1. Introduction

Tetrachloride liquids possessing a high degree of symmetry in three dimensions offer themselves as an interesting group of two-component systems for neutron and x-ray diffraction study. Thus, attempts have been made by various workers to account for the molecular structure function (Egelstaff *et al* 1971; Narten 1976; van Tricht 1977a; Granada *et al* 1979) in this direction in the recent past. In the vanadium tetrachloride molecule, the central vanadium atom makes negligible contribution to the diffraction pattern, as the scattering amplitude of vanadium is -0.41 fm (1 fm = 10^{-13} cm) in comparison to the chlorine atom scattering amplitude of 9.58 fm, and this makes the study simpler while one attempts to obtain partial distributions of constituent atoms.

The existence of orientational correlation in molecular liquids have been established by several workers (Egelstaff *et al* 1971; Powles 1973; Sandler *et al* 1974; Gibson and Dore 1979; Murad *et al* 1979). Gibson and Dore (1979) have concluded that in VCl_4 , strong correlation between neighbouring molecules exist due to non-sphericity of the molecule.

In this paper, we use the Apollo model of Egelstaff *et al* (1971) as a basis for

bond of one molecule is in line with that of the other molecule and the chlorine atom of one lies in the hollow formed by the three off axis chlorines of the second. If it is assumed that the orientation of one molecule to the other is statistically independent of their relative separation, one can then uncouple the radial and angular correlations of the two molecules. Though, this is only an approximation, several workers (Page and Powles 1971; Suzuki and Egelstaff 1974; Gopala Rao and Joardar 1979, 1980) have assumed this separation in their work and in fact such a separation in the case of methane (Murad *et al* 1979) works very well as they put it. In general, the results are good, when the distance between the molecular centres is large. However, at short distances between the molecules, where the correlations are large the interlocking of two molecules makes it probably difficult for rotations to occur independent of translations and thus the uncoupling of radial and angular correlations is not exact. In the first part of this work, the motto is to generate theoretically the molecular structure function, $S_m(Q)$. The centre structure function, $S_c(Q)$ has been computed with hard sphere model and the approximation of free rotation is accounted by taking a third term which we call as a decoupling correction term. The idea of such an additional term in the expression for $S_m(Q)$ was also given earlier by Egelstaff *et al* (1971) and Weis and Levesque (1976). The molecular structure function thus obtained is compared with the experimental results of Gibson and Dore (1979).

In the neutron diffraction study of VCl_4 molecule, the contribution of the central vanadium atom scattering to the total intensity being negligibly small, the diffraction pattern is effectively from hollow tetrahedral chloride units. Thus it behaves like a homonuclear system which enables to extract out the chlorine-chlorine partial pair distribution function, $g_{\text{Cl-Cl}}(r)$, from the neutron data (Gibson and Dore 1979). From this, we evaluate the chlorine-chlorine partial structure, $S_{\text{Cl-Cl}}(Q)$, the intermolecular chlorine-chlorine direct correlation function, $C_{\text{Cl-Cl}}(r)$, which is analogous to the function, $C_{\alpha\gamma}(r)$ in the reference interaction site model (RISM) theory (Lowden and Chandler 1973) and also the intermolecular chlorine-chlorine angle-averaged potential function $\phi_{\text{Cl-Cl}}(r)$, through a method given by Gopala Rao and Joardar (1978a).

In the second part of the paper, to get an approximate idea of the potential governing the molecular centres, we assume that to a first approximation equation (3) holds and from experimental $S_m(Q)$, we deduce the $S_c(Q)$ function. It may be pointed out that in the present molecule, the vanadium atom lying at the centre of mass of the system, the $S_c(Q)$ function represents the vanadium-vanadium partial structure, $S_{\text{V-V}}(Q)$. From $S_{\text{V-V}}(Q)$, we evaluate the centre radial distribution function, $g_{\text{V-V}}(r)$, the centre direct correlation function, $C_{\text{V-V}}(r)$, and the angle-averaged intermolecular potential function (or the vanadium-vanadium potential) $\phi_{\text{V-V}}(r)$.

2. Theory

The molecular structure function, $S_m(Q)$, may be written as

scattering lengths of the i th and j th nuclei, which are separated by a distance r_{ij} . The angular bracket denotes an ensemble average and the summation extends over all pairs of nuclei in the system. The contributions to the summation arising from atoms within the same molecule may be separated out of the molecular structure function so that

$$S_m(Q) = f_1(Q) + D_m(Q), \quad (2)$$

where $f_1(Q)$ is the molecular form factor and $D_m(Q)$ corresponds to the inter-molecular contributions. At large Q values, $D_m(Q)$ becomes negligible and the observed diffraction pattern is characteristic of a single molecule. At small Q values, the $D_m(Q)$ function is more prominent and gives information about the liquid structure.

The term, $D_m(Q)$ can be approximately separated into a molecular centre structure function term, $S_0(Q)$ and an orientation dependent form factor, $f_2(Q)$, such that

$$S_m(Q) = f_1(Q) + f_2(Q) [S_0(Q) - 1]. \quad (3)$$

However, as discussed earlier, this is only a rough approximation though several workers (Page and Powles 1971; Suzuki and Egelstaff 1974; Gopala Rao and Joardar 1979, 1980) have found it to be good to explain certain liquid structures. Particularly in a molecule like VCl_4 , where the non-sphericity is large, the above relation (3) fails to account for the molecular structure. The addition of a third term, $f_3(Q)$, is required to give a proper description of the molecular structure function, thus

$$S_m(Q) = f_1(Q) + f_2(Q) [S_0(Q) - 1] + f_3(Q) \quad (4)$$

where we call $f_3(Q)$ as the decoupling correction term and this gives a measure of the orientational correlation between the molecules in the system.

For tetrahedral VCl_4 molecule, the molecular form factor, $f_1(Q)$, is given by

$$f_1(Q) = (b_V + 4b_{\text{Cl}})^{-2} [b_V^2 + 4b_{\text{Cl}}^2 + 8b_V b_{\text{Cl}} j_0(Qr_{\text{V-Cl}}) + 12b_{\text{Cl}}^2 j_0(Qr_{\text{Cl-Cl}})] \quad (5)$$

where b_V and b_{Cl} are the coherent scattering lengths for the vanadium and chlorine atoms respectively, $j_0(Qr)$ is a spherical Bessel function of zeroth order and $r_{\text{V-Cl}}$ and $r_{\text{Cl-Cl}}$ are the appropriate distances between the vanadium and chlorine nuclei.

For the orientation dependent term, $f_2(Q)$, we use Egelstaff's Apollo model for tetrachloride liquids (Egelstaff *et al* 1971), where $f_2(Q)$ is given by

$$f_2(Q) = (b_V + 4b_{\text{Cl}})^{-2} [b_V^2 + 8b_V b_{\text{Cl}} j_0(Qr_{\text{VCl}}) + b_{\text{Cl}}^2 + 6b_{\text{Cl}}^2 j_0(Qr_{\text{Cl-Cl}}) + 9b_{\text{Cl}}^2 I(Qr_t)] \quad (6)$$

where

$$I(Qr_t) = \int_0^{\pi/2} I_0^2(Qr_t \sin \theta) \sin \theta d\theta$$

Q_0 is a Bessel function of zeroth order. We assume $S_c(Q)$ to be that given by Percus-Yevick approximation for hard sphere potential.

The term $f_3(Q)$, used to make up the discrepancy of equation (3) in accounting for the observed $S_m(Q)$, is taken to be in the following form :

$$f_3(Q) = \frac{\sin \{\lambda_1 (Q_0 - Q)\}}{\lambda_2 (Q_0 - Q)}, \quad (7)$$

where λ_1 and λ_2 are two parameters, λ_1 being angular and λ_2 radial in nature. This function is a short range function and becomes almost zero at large Q values and also when $Q \rightarrow 0$. Thus in the long wave limit ie as $Q \rightarrow 0$, $f_3(Q)$ gives a limiting value of 0.01 and for large Q , $f_3(Q)$ becomes vanishingly small. Though $f_3(Q)$ term cannot be derived rigourously from theory, it can be formulated intuitively. Thus out of the two parameters one stands for the radial part and the other for the angular part of the correlations.

At this juncture it may be pointed out that several other mathematical forms were tried for the term $f_3(Q)$ and these are mentioned below.

$$(i) f_3(Q) = \frac{1}{(4\pi T)^{1/2}} \exp [-(Q - Q_0)^2/4\tau]. \quad (8)$$

Here τ is a parameter and Q_0 is the point where the decoupling correction is the highest.

$$(ii) f_3(Q) = \exp(-\lambda Q) \sin \lambda Q, \quad (9)$$

where λ is a parameter.

$$(iii) f_3(Q) = \lambda Q^n \exp(-\lambda Q^n), \quad (10)$$

where λ and n are parameters. Equations (8)-(10) were used with several variations and were found to be inferior to equation (7) in accounting for $S_m(Q)$.

The total pair-distribution function, $g(r)$, in two-component system like VCl_4 is the sum of three partial components corresponding to the intramolecular, $g_m(r)$ and intermolecular, $g_L(r)$ components :

$$g(r) = g_m(r) + g_L(r). \quad (11)$$

But since the terms depending on the position of the vanadium atom, due to its very small scattering length, are negligible, the intermolecular pair distribution function, $g_L(r)$, is approximated by :

$$g_L(r) \simeq g_{Cl-Cl}(r). \quad (12)$$

and is obtained by the Fourier transformation of $D_m(Q)$, such that

$$g_{Cl-Cl}(r) - 1 = \frac{2}{\pi^2 \rho_{Cl} r} \int_0^{Q_{max}} Q D_m(Q) M(Q) \sin Qr dQ \quad (13)$$

where ρ_{Cl} is the chlorine number density and $M(Q)$ is a Lorch modification function introduced into the transformation in order to reduce termination effects and is given by

$$M(Q) = \frac{\sin(\pi Q/Q_{\text{max}})}{(\pi Q/Q_{\text{max}})}.$$

From equation (10), the chlorine-chlorine partial structure, $S_{\text{Cl-Cl}}(Q)$, which is the Fourier transform of $g_{\text{Cl-Cl}}(r)$, can be found out to be

$$S_{\text{Cl-Cl}}(Q) = 4D_m(Q) + 1 \quad (14)$$

From $S_{\text{Cl-Cl}}(Q)$, the effective chlorine-chlorine potential can be obtained (Gopala Rao and Joardar 1978a).

As already stated, assuming equation (3) holds good as a first approximation we deduce $S_o(Q)$ from the experimental $S_m(Q)$, and subsequently from $S_o(Q)$, other quantities like $g_{\text{V-V}}(r)$, $C_{\text{V-V}}(r)$ and $\phi_{\text{V-V}}(r)$ can be obtained (Gopala Rao and Joardar 1978a).

3. Results and discussion

The molecular structure of VCl_4 molecule has been investigated by Morino and Uehara (1966) using gas phase electron diffraction. The study has shown that the tetrahedral symmetry of the molecule is not disturbed by vibronic interactions. Even in the condensed liquid state the spherical symmetry of the molecule may be assumed to exist still to a good approximation and therefore we choose to calculate the centre structure factor, $S_o(Q)$ through a simple Percus Yevick approximation for the hard sphere potential with a hard sphere diameter, $\sigma = 5.50 \text{ \AA}$. In this connection, it may be pointed out that $S_o(Q)$ generated with a Sutherland's potential as a perturbation over the hard sphere in the random phase approximation has been found not to improve the results over the simple hard sphere. This choice of σ is based on the molecular dynamics calculation on VCl_4 liquid with a Lennard-Jones potential by Murad and Gubbins (1980), who get the $g_{\text{V-V}}(r)$ peak at $r = 6.30 \text{ \AA}$. To get σ from this, we make use of the approximate relation $\sigma_{\text{LJ}} = 2^{1/6} \sigma_{\text{HS}}$. This value of $5.50 \text{ \AA}$ compares well with the σ value of $5.57 \text{ \AA}$ for a similar molecule like TiCl_4 , given by van Tricht (1977b). The $f_1(Q)$ and $f_2(Q)$ were calculated through equations (5) and (6) respectively. These are plotted in figure 1. The molecular parameters used are taken from Gibson and Dore (1979) and are tabulated below along with other parameters.

Temperature, $T = 294^\circ \text{K}$

Molecular number density, $\rho = 0.00565 \text{ \AA}^{-3}$

Hard sphere diameter, $\sigma = 5.50 \text{ \AA}$

$r_{\text{V-Cl}} = 2.14 \text{ \AA}$, $r_{\text{Cl-Cl}} = 3.49 \text{ \AA}$

The experimental $S_m(Q)$ data for a neutron wavelength of 0.71 Å were reproduced by Fourier transforming the real space distribution, $d_L(r)$, data (where $d_L(r) = 4\pi r \rho_{Cl} [g_{Cl-Cl}(r) - 1]$) obtained by Gibson and Dore (1979).

In figure 2, we give $f_3(Q)$ as obtained from equation (7). The parameters λ_1 and λ_2 were chosen so as to give the best possible fit of $S_m(Q)$ as given by equation (4).

Now, as mentioned earlier, the total intermolecular scattering is effectively from chlorine atoms and thus the chlorine-chlorine partial structure, $S_{Cl-Cl}(Q)$ is obtained from $D_m(Q)$ through equation (11). This $S_{Cl-Cl}(Q)$ function and the effective intermolecular chlorine pair potential, $\phi_{Cl-Cl}(r)$ has been obtained and presented in figures 4 and 5 respectively. In figure 6, the $g_{Cl-Cl}(r)$ and $C_{Cl-Cl}(r)$ functions are also shown.

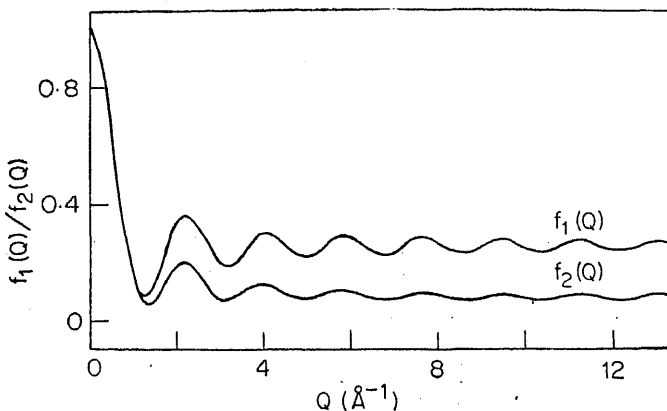
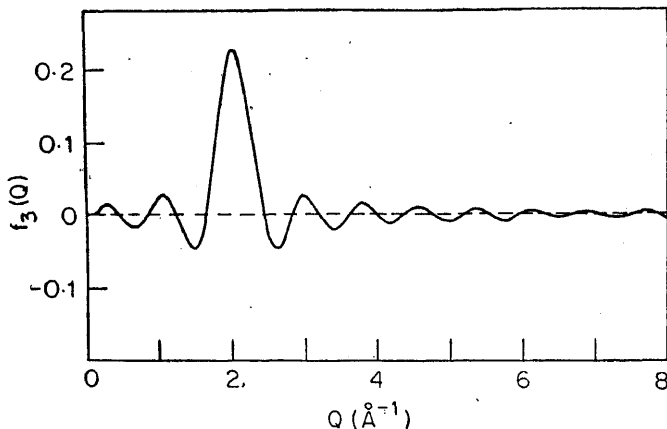


Figure 1. The intramolecular form factor, $f_1(Q)$ and the intermolecular form factor, $f_2(Q)$.



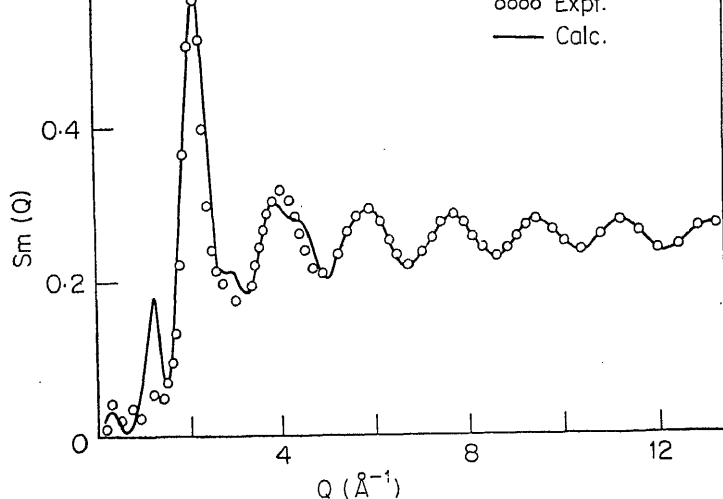


Figure 3. The molecular structure function, $S_m(Q)$.

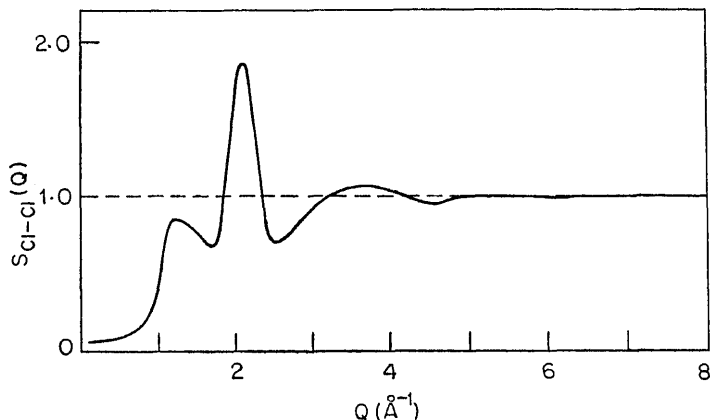


Figure 4. The chlorine-chlorine partial structure functions $S_{Cl-Cl}(Q)$.

Figure 7 gives the centre structure, $S_{V-V}(Q)$ evaluated through the approximate equation (3) obtained from the experimental $S_m(Q)$. Figure 8 gives the inter-molecular potential $\phi_{Cl-Cl}(r)$ and figure 9 the $g_{V-V}(r)$ and $C_{V-V}(r)$ functions, all obtained from $S_{V-V}(Q)$.

Figure 2 gives an idea of the contribution of the $f_3(Q)$ correction term to the total molecular structure function. At the principal peak for $S_m(Q)$, this contribution is 0.22 out of 0.56, *i.e.*, about 39%. Unlike in methane (Murad *et al* 1979), the large central vanadium atom in VCl_4 makes the chlorine atoms more protruding, thereby increasing the non-sphericity and thus the orientations of the molecules in the Apollo model are likely to be strong, which inhibits the free rotation of the molecules with respect to each other independent of trans-

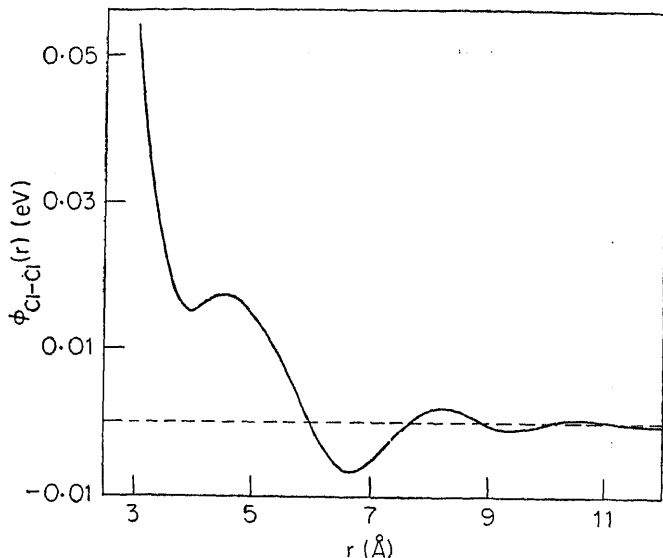


Figure 5. The intermolecular chlorine-chlorine potential function, $\phi_{Cl-Cl}(r)$.

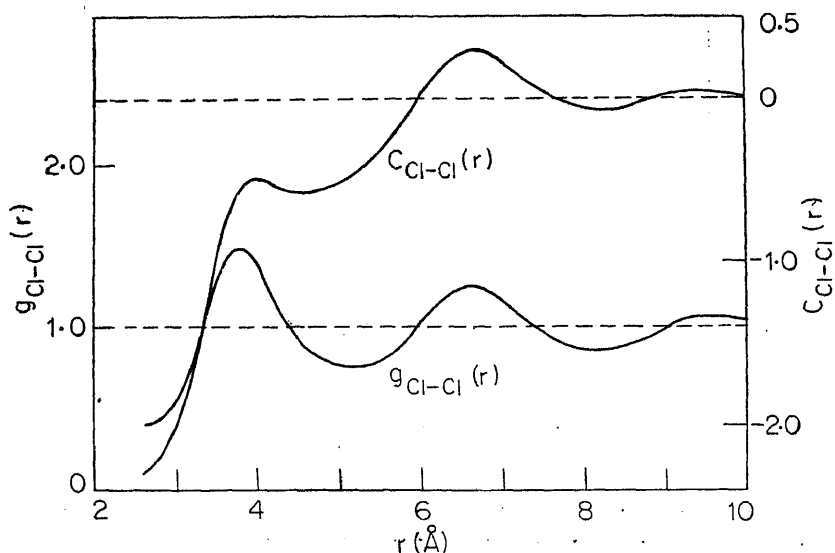


Figure 6. The chlorine-chlorine direct correlation function, $C_{Cl-Cl}(r)$ and the chlorine-chlorine pair distribution function, $g_{Cl-Cl}(r)$.

The addition of such a correction term gives a molecular structure function, which is given in figure 3 and compared with experimental $S_m(Q)$ data. The $S_m(Q)$ so obtained compares reasonably well with the experimental one, except giving a satellite peak with a height of 0.18 at $Q = 1.3 \text{ \AA}^{-1}$. The experimental results

may be pointed out that other tetrachlorides like SiCl_4 , and TiCl_4 show such pronounced satellite peaks corresponding to this point (van Tricht 1977b).

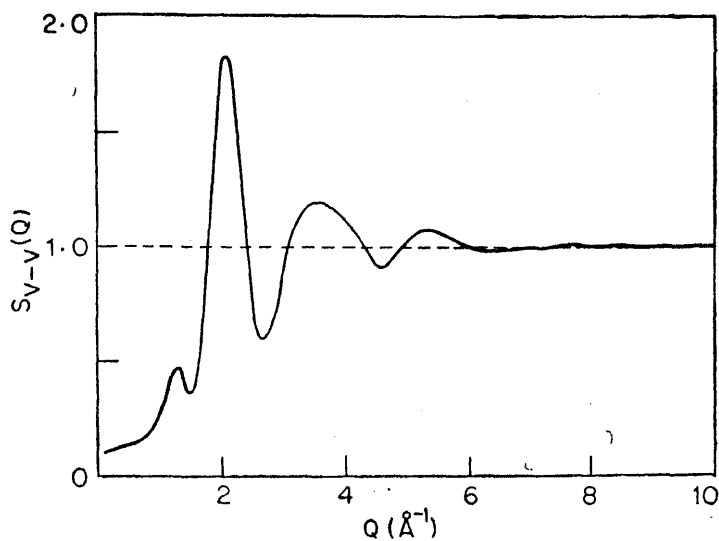
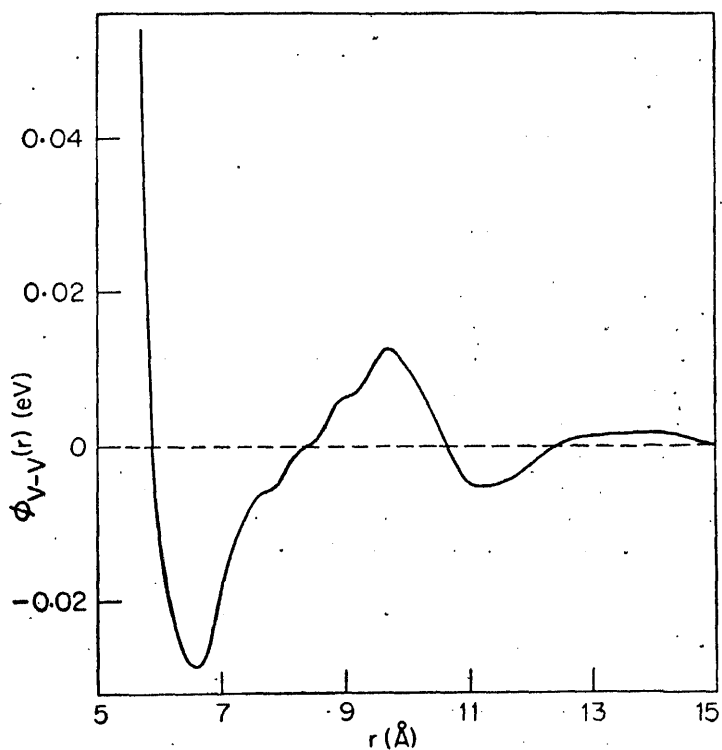


Figure 7. The vanadium-vanadium partial structure functions, $S_{V-V}(Q)$.



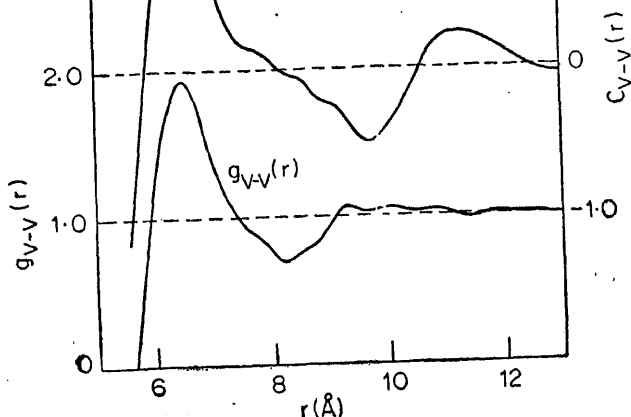


Figure 9. The vanadium-vanadium direct correlation function, $C_{V-V}(r)$, and the vanadium-vanadium pair distribution function $g_{V-V}(r)$.

It is seen from figure 5 that at the nearest neighbour distance, *i.e.*, 3.95 Å, for the chlorine atoms, the potential has a positive value of 1.52×10^{-2} eV. It may be pointed out here that liquid chlorine also gives such a positive minimum (Gopala Rao and Joardar 1978b) in its potential function. However, the second neighbour rests at a negative potential well of depth 0.66×10^{-2} eV at a distance of 6.65 Å. The potential dies very fast and thus the chlorine-chlorine interactions are weak beyond the second neighbour distance.

The centre structure, $S_c(Q)$, shown in figure 7, also has a subsidiary peak at a Q value 1.5 Å^{-1} , like the calculated molecular structure function. The oscillations in it almost vanish beyond $Q = 6.0 \text{ Å}^{-1}$. The intermolecular potential function, $\phi_{V-V}(r)$ in figure 8 gives an equilibrium distance between the molecular centres of 6.55 Å, and the potential depth at this point is 2.84×10^{-2} eV.

The study shows that the present orientational model can explain the molecular structure of liquid VCl_4 , if we introduce a correction factor for the separation of the radial and angular part in the intermolecular scattering term. This term plays a significant role in explaining the molecular structure for tetrahedral molecules where the sphericity has been lost to a great extent by the large size of the central and peripheral atoms. However, for molecules like CH_4 and CCl_4 which are more spherical and where positional correlations dominate over orientational correlations (Murad *et al* 1979; Gopala Rao and Murty 1974, 1976) the role of this term will be diminished. Here it is pertinent to point out that Murad *et al* (1979) have found the free rotation approximation is superior to the Reference Interaction Site Model (RISM) theory in explaining the structure of the tetrahedral liquid methane molecule,

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Periodic precipitation of cobalt(II) oxinate in agar gel : factors influencing the flocculation

N KANNIAH, S AMBROSE, F D GNANAM and P RAMASAMY*

A C College of Technology, Perarignar Anna University of Technology,
Madras 600 025, India

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Abstract. The influence of concentration, ageing and pH of the gel medium on the periodic precipitation of cobalt oxinate in agar gel is reported. The results are explained on the basis of Shinohara's revised flocculation theory. The flocculation value (F) increases with increase in the gel concentration whereas it decreases with increase in ageing and pH of the gel. The raise in temperature of the gel increases the solubility of the sparingly soluble substance and hence the F value. The effect of additives on the periodic precipitation of cobalt(II) oxinate is reported.

Keywords. Periodic precipitation; cobalt oxinate; flocculation value; gel concentration; ageing.

1. Introduction

Many compounds that form insoluble precipitates in a counter diffusion system exhibit the Liesegang (1896) phenomenon in which a series of concentric rings are produced rather than a continuous precipitate. Few quantitative data are available despite over 800 publications on this subject (Stern 1967). The formation of Liesegang rings has been influenced by various factors like concentration of the reactants, concentration, ageing, temperature and pH of the gel medium and the amount of additives present.

We have recently published the experimental conditions for obtaining the Liesegang rings of cobalt(II) oxinate in agar and the influence of the concentration of the reactants on the periodic precipitation (Kanniah *et al* 1981). In this paper the influence of the concentration, ageing, pH and temperature of the gel and the effect of additives on the formation of Liesegang rings of cobalt oxinate are discussed in detail.

2. Theory

The periodic precipitation of cobalt oxinate has been explained on the basis of the revised coagulation theory of Shinohara (1970). As the outer electrolyte—

* To whom correspondence should be made.

formed as a sol at the contact plane of the two reactants. This boundary known as sol-front advances spreading the sol region. As more and more outer electrolyte diffuses, the ionic concentration reaches a characteristic value Γ which triggers the flocculation of the sol. Γ is expressed by the equation

$$\Gamma = C_{10} \left[1 - \frac{G(k_1)}{G(k)} \right], \quad (1)$$

where C_{10} is the concentration of cobalt nitrate

$$G(k) = \frac{1}{(2\pi)^{1/2}} \int_0^k \exp\left(-\frac{1}{2}\eta^2\right) d\eta, \quad (2)$$

$$k_1 = k/p \text{ and } p = \frac{x_{n+1}}{x_n}, \quad (3)$$

p is known as the spacing coefficient. x_{n+1} and x_n are the positions of the $(n+1)$ th and n th rings from the gel boundary. k is called the front constant which is estimated using the Adair's equation. The concentration of the super-saturated solution of the product (C_{30}) formed just before the formation of sol is given by

$$C_{30} = C_{10} \frac{\exp(-k^2/2)}{(2\pi)^{1/2} k G(k)} \quad (4)$$

The flocculation value F is calculated as

$$F = C_{30} + \Gamma. \quad (5)$$

3. Experimental

3.1. Effect of gel concentration

2.178 grams of analytical grade oxine were dissolved in minimum amount of 2N acetic acid. This solution was mixed with hot agar agar solution and the final volume was made up to 300 ml. The pH of the solution was adjusted to 4.25. Thus 1.0% agar agar solution impregnated with 0.05 mole/lit oxine was prepared at 4.25 pH. 50 ml of this solution was poured into a corning tube of 20 mm diameter and allowed to set. After 3 hr 10 ml of 1.031 mole/l cobalt nitrate was taken over the gel. To study the effect of gel concentration of the periodic precipitation of cobalt oxinate, the gel concentration was varied from 0.4% to 2.0%. In all the experiments the concentration of the inner electrolyte and that of the outer electrolyte was kept as 0.05 and 1.031 mole/l respectively.

3.2. Effect of ageing of the gel

1% agar agar gel impregnated with 0.05 mole/l oxine was prepared as before. 1.031 mole/l cobalt nitrate was taken over the set gel at different time. The

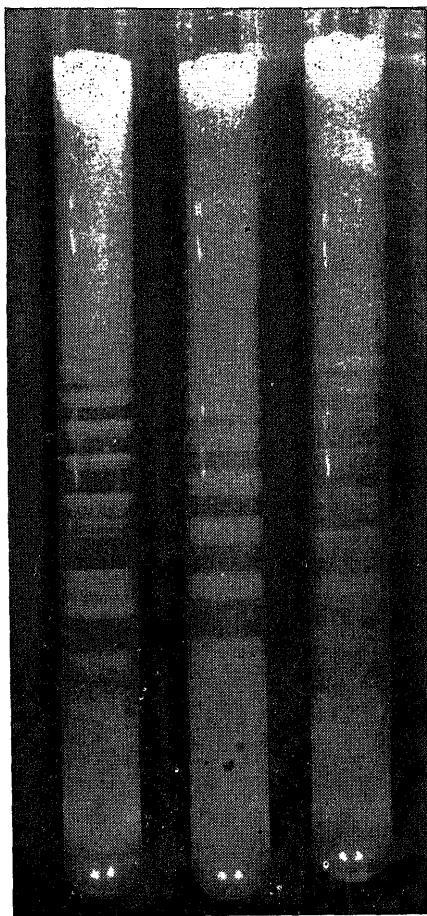


Figure 1. The Liesegang rings of cobalt oxinate in agar gel in presence of additives potassium sodium tartarate, potassium thiocyanate and potassium chloride.

The periodic precipitation of cobalt oxinate was normally carried out at room temperature (30°C). The influence of the temperature was studied by keeping the gel at different temperatures. The glass tubes containing the hot gel solution with oxine were immersed in a thermostat kept at the required temperature. The temperature of gel was varied from 30 to 42°C. In all these experiments the concentrations of the gel, oxine and cobalt nitrate was 1%, 0.05 mole/l and 1.031 mole/l respectively.

3.4. *The effect of pH of the gel medium*

Oxine was dissolved in minimum amount of 2N acetic acid and the hot agar agar solution was mixed. The pH of this solution was adjusted with aqueous ammonia to 4.25. Similarly the pH of the gel solution with oxine was varied from 3.7 to 4.7. Oxine is precipitated, when the pH is above 4.7. When the pH was below 3.7 gel set was not observed. The pH of the solution was measured at 60°C. The gel solutions were allowed to set at room temperature (30°C) and cobalt nitrate solution was taken over the set gel after 3 hr. The concentrations of gel, oxine and cobalt nitrate were the same as in the previous experiment.

3.5. *Influence of additives*

To study the effect of additives on the periodic precipitation of cobalt oxinate, suitable additives were taken along with oxine in the gel medium. The amount of additive was varied from 0.001 to 0.026 mole/l. When the gel containing oxine and additive was set, cobalt nitrate was taken as the outer electrolyte. The concentrations of the gel, inner electrolyte and outer electrolyte were kept as 1.0%, 0.05 and 1.031 mole/l respectively. Potassium sodium tartarate, potassium chloride and potassium thiocyanate are the additives taken along with oxine in the gel.

In all the experiments, sharp brown coloured disc-like precipitate rings demarcated by clear void spaces were obtained within a week (figure 1). The interspacing between successive rings increases with the number of ring (n) from the gel boundary. At the lower rings, small crystals of cobalt oxinate were observed. The distance measurements were made with cathetometer. The IBM 1130 computer was used for the calculation of flocculation values using Shinohara's coagulation theory.

4. Results and discussion

4.1. *Effect of concentration of the gel medium*

Matalon and Packter (1955) have established that the gel has a great influence on the periodic precipitation of insoluble salts and that the gel interacts appreciably with the precipitated substance. They have modified Wager's relation (1950) and derived the following equation:

where C_g = concentration of the gel; B = a constant which is a measure of supersaturation of sparingly soluble substance; m = a constant with integral value; and C_{10} = outer electrolyte concentration.

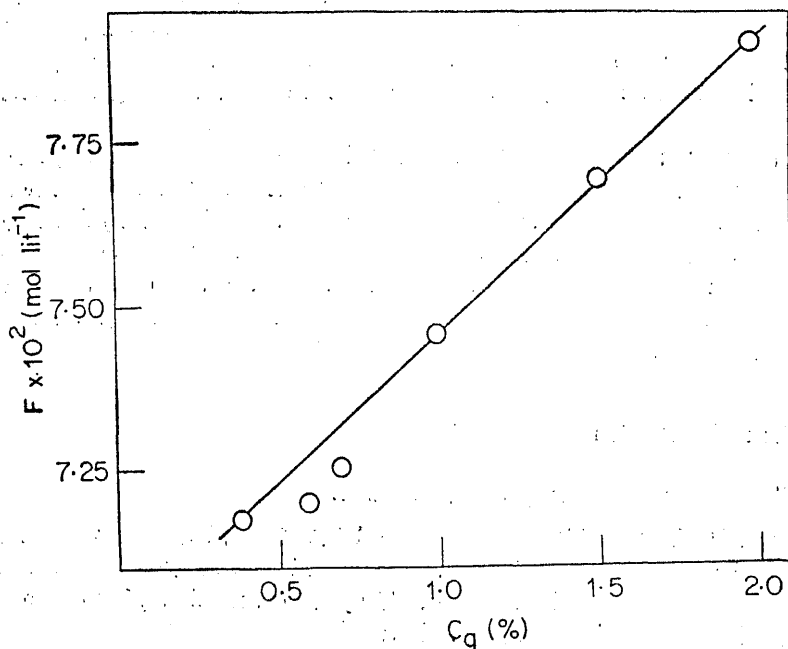
From the above equation it is very clear that the spacing coefficient (p) will increase with increase in the gel concentration. As the concentration of gel increases the interaction of the gel with the precipitated substance increases. Hence the sol of the sparingly soluble substance is well protected. The stability of the sol increases. Therefore the amount of the outer electrolyte required to flocculate the sol will be more. Thus the flocculation value must increase with increase in the gel concentration (figure 2) leading to an increase in the spacing coefficient (p).

4.2. Effect of ageing of the gel

During ageing of the gel the micellae and the intervening capillary spaces become coarser. This will decrease the solubility of cobalt oxinate leading to rapid precipitation. Hence the flocculation value (figure 3) decreases with increase in the ageing of the gel.

4.3. Effect of temperature

The increase in temperature of gel leads to a progressive diminution of the total volume of the micellae (Clayton 1932). Hence the pore size increases. This in turn leads to an increase in the diffusion coefficient. Moreover the solubility of



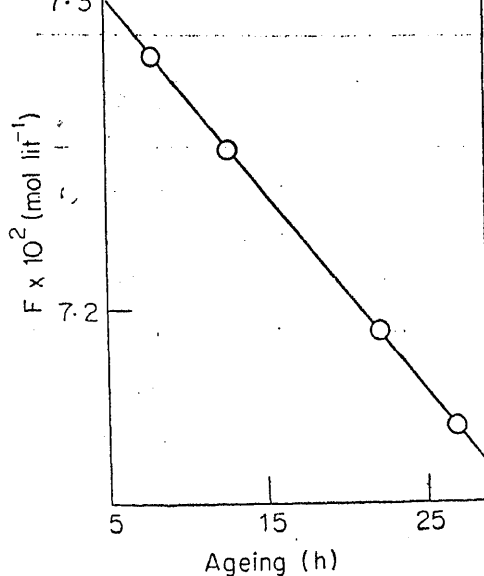


Figure 3. Effect of ageing on the flocculation value (F). $C_{30} = 1.031$ mole/l; $C_{20} = 0.05$ mole/l, $C_p = 1\%$.

the sparingly soluble product increases with increase in temperature. As the solubility increases the precipitation takes a longer time and hence the rings are formed at greater distances leading to an increase in the spacing coefficient. As the solubility increases, the concentration of the supersaturated solution (C_{30}) formed just before flocculation increases leading to a higher flocculation value (F). Hence increase in temperature of the gel medium increases the flocculation value (table 1).

4.4. Effect of pH of the gel medium

The pH of the gel medium plays a predominant role in the periodic precipitation of the sparingly soluble salts (Varma 1953). Cobalt oxinate is soluble in acids. As the pH of the gel medium increases, the solubility decreases leading to a decrease in the spacing coefficient and flocculation value (table 2). The periodic precipitation of cobalt oxinate is observed only in the narrow range of pH 4.3 to 4.0.

4.5. Effect of additives

The characteristic features of the periodic precipitation of cobalt oxinate are very much influenced by the presence of additives. The effect of impurities on the periodic precipitation of calcite has been studied by Bugazh and Fraknoy (1961), Gnanam *et al* (1980) and Krishnan *et al* (1981). When potassium sodium tartrate, potassium thiocyanate and potassium chloride are used as additives, the flocculation value increases with increase in the concentration of the impurity. This reveals that solubility of the sparingly soluble product increases with increase

Table 1. Effect of temperature on flocculation value.

C_{10} mole/l	C_{20} mole/l	Temperature °C	p	$F \times 10^3$ mole/l
1.031	0.05	30	1.049	7.038
1.031	0.05	34	1.058	7.380
1.031	0.05	38	1.064	7.426
1.031	0.05	42	1.082	7.897
0.859	0.05	30	1.051	7.035
0.859	0.05	34	1.061	7.126
0.859	0.05	38	1.065	7.212
0.859	0.05	42	1.085	7.658
0.687	0.05	30	1.053	6.997
0.687	0.05	34	1.065	6.983
0.687	0.05	38	1.071	7.093
0.687	0.05	42	1.090	7.425
0.515	0.05	30	1.059	7.067
0.515	0.05	34	1.071	6.881
0.515	0.05	38	1.075	6.926
0.515	0.05	42	1.097	7.227

Table 2. Effect of pH on flocculation value.

pH	C_{10} mole/l	C_{20} mole/l	p	$F \times 10^3$ mole/l
4.05	1.031	0.05	1.101	8.412
4.20	1.031	0.05	1.092	8.167

impurities the flocculation value is the lowest in the case of potassium

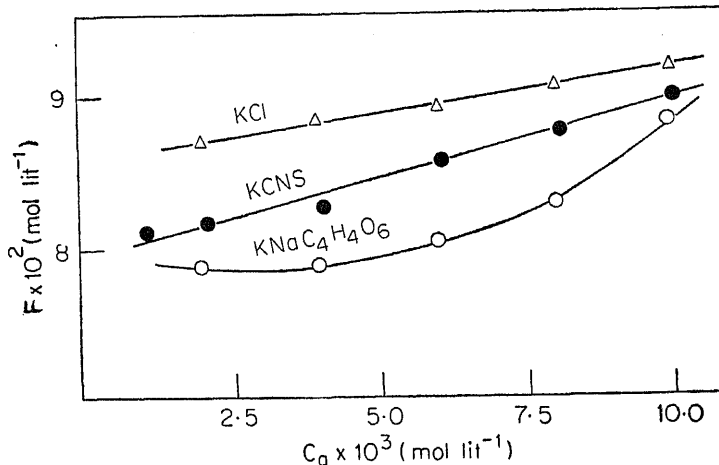


Figure 4. Effect of additives on the flocculation value (F). $C_{10} = 1.031 \text{ mole/l}$; $C_{20} = 0.05 \text{ mole/l}$, $C_p = 1\%$; C_a = concentration of additives.

When excess cobalt nitrate diffuses into a gel impregnated with oxire, a positively charged sol of cobalt oxinate is formed due to the adsorption of excess Co^{2+} ion. In that case the counter-ion plays an important role in flocculating the sol. Among the counter-ions (tartarate, thiocyanate and chloride), the tri-valent tartarate will be more effective in flocculating the sol. Hence the flocculation value should be the lowest for a particular concentration of the tartarate. This can also be accounted by the lyotropic order of anions (McBain 1950).

5. Conclusion

The results thus conclusively prove that the concentration, ageing, pH and temperature of the gel have pronounced influence on the flocculation of cobalt oxinate. The flocculation values of different anions are in the lyotropic order.

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Bis (η^5 -cyclopentadienyl/indenyl) N-aryl dithiocarbamato chloro oxotungsten(VI) complexes

G S SODHI, H S SANGARI and N K KAUSHIK*

Department of Chemistry, University of Delhi, Delhi 110007, India

MS received 16 October 1981 ; revised 24 December 1981

Abstract. Some bis(η^5 -cyclopentadienyl) N-aryl-dithiocarbamato chloro oxotungsten (VI) complexes of the type $(C_5H_5)_2WO(S_2CNHR)Cl$ ($R = o$ -, m -, p -tolyl and Ph) have been prepared by the reaction of stoichiometric amounts of bis (η^5 -cyclopentadienyl) oxotungsten(VI) dichloride with sodium salts of dithiocarbamic acids in refluxing tetrahydrofuran. The corresponding indenyl complexes of the type $(C_9H_7)_2WO(S_2CNHR)Cl$ were similarly synthesised by refluxing equimolar quantities of bis(η^5 -indenyl) oxotungsten(VI) dichloride and sodium dithiocarbamate in tetrahydrofuran. Infrared spectral studies demonstrate that in these complexes dithiocarbamate ligands are bidentate. Electronic spectra, magnetic susceptibility and elemental analysis have also been carried out for the complexes.

Keywords. Cyclopentadienyl; indenyl; oxotungsten(VI); sodium dithiocarbamates.

1. Introduction

In earlier papers, we reported cyclopentadienyl (Sangari *et al* 1980) and indenyl (Kaushik *et al* 1980) derivatives of oxomolybdenum(VI) complexes. Our interest in the investigation of bonding mode of various dithiocarbamate ligands (Sangari *et al* 1981) prompted us to synthesise and characterise a number of organo oxotungsten(VI) dithiocarbamates.

2. Experimental

2.1. Materials

Sodium dithiocarbamates were prepared by standard method (Klöpping *et al* 1951). Bis (η^5 -cyclopentadienyl) and bis (η^5 -indenyl) oxotungsten(VI) dichloride were prepared by the interaction of tungsten(VI) oxytetrachloride with sodium cyclopentadienyl and sodium indenyl respectively (Anand *et al* 1968).

* To whom correspondence should be made.

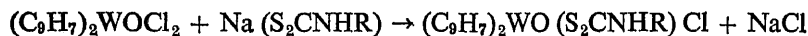
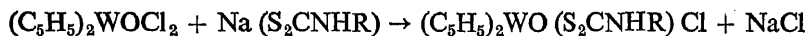
spectrophotometer. The electronic spectra were recorded on a Perkin-Elmer 4000 Å instrument in the 450–700 nm range. Magnetic susceptibilities at room temperature were measured on a standard Gouy's balance. Mercury tetrathiocyanatocobaltate (II) was used as calibrant.

2.3. Preparation of the complexes

The complexes were obtained as insoluble products after refluxing bis (η^5 -cyclopentadienyl/indenyl) oxotungsten(VI) dichloride with stoichiometric amounts of sodium dithiocarbamate for 14–18 hr. The yellowish-brown to brown complexes were filtered, washed successively with tetrahydrofuran, acetone and water and finally recrystallised from petroleum ether.

3. Results and discussion

Bis (η^5 -cyclopentadienyl/indenyl) oxotungsten(VI) dichloride reacts with sodium dithiocarbamates in equimolar quantities according to the following general equations :



(where R = *o*-, *m*-, *p*-tolyl and Ph).

The method used to prepare all the oxotungsten(VI) complexes gave materials of good purity as evidenced by satisfactory elemental analysis (table 1) and IR studies (table 2).

All the oxotungsten(VI) complexes are soluble in hot petroleum ether but insoluble in most organic solvents. They are quite stable in air. Their decomposition and melting points are very high, *i.e.*, above 300°C. They are yellowish brown to brown in colour. Magnetic susceptibility value at room temperature shows that all compounds are diamagnetic.

3.1. Infrared spectra

The main interest in the preparation of these complexes is the attachment of the dithiocarbamate ligand. If the dithiocarbamate ligand is bidentate, a single band at $\sim 1000\text{ cm}^{-1}$ is found (Bonati *et al* 1967) which is due to two equivalent C–S stretching vibrations. In unidentate dithiocarbamate, as in $\text{Ru}(\text{NO})(\text{S}_2\text{CNEt}_2)_3$ (Domenicano *et al* 1966) a doublet arises at $\sim 1005\text{ cm}^{-1}$ and 983 cm^{-1} which is due to two non-equivalent C–S stretching vibrations. Thus this a reliable criterion for determining the bonding mode of the dithiocarbamate ligand. All the prepared complexes possess one medium intensity band at $\sim 1000\text{ cm}^{-1}$. This indicates the presence of four-membered ring system in these complexes and also supports

Table 2. Characteristic infrared bands (cm⁻¹)

Complex	ν (W-Cl)	ν (W-S)	ν (W=O)	ν (C $\cdots$ N)	ν (C-S)	ν (C-H) stretching band	ν (C-O) asym-metric ring breathing	ν (C-H) in plane bending	ν (C-H) out of plane bending
(C ₆ H ₅) ₂ WO(S ₂ CNHn-CH ₃ C ₆ H ₄)Cl	360m	355m	965m	1520s	1025s	3015m	1435m	1045vs	823
(C ₆ H ₅) ₂ WO(S ₂ CNHm-CH ₃ C ₆ H ₄)Cl	365m	350m	950m	1510s	1015s	3005m	1425m	1040vs	833
(C ₆ H ₅) ₂ WO(S ₂ CNH-CH ₃ C ₆ H ₄)Cl	370m	350m	955m	1505s	1020s	3000m	1430m	1050vs	822
(C ₆ H ₅) ₂ WO(S ₂ CNHC ₆ H ₅)Cl	360m	340m	960m	1515s	1015s	3010m	1435m	1055vs	822
(C ₆ H ₅) ₂ WO(S ₂ CNHn-CH ₃ C ₆ H ₄)Cl	365m	345m	945m	1506s	1000s	3030m	1430m	1040vs	833
(C ₆ H ₅) ₂ WO(S ₂ CNHm-CH ₃ C ₆ H ₄)Cl	370m	340m	955m	1505s	1015s	3005m	1445m	1050vs	822
(C ₆ H ₅) ₂ WO(S ₂ CNH-CH ₃ C ₆ H ₄)Cl	365m	345m	950m	1500s	1000s	3000m	1425m	1055vs	822
(C ₆ H ₅) ₂ WO(S ₂ CNHC ₆ H ₅)Cl	360m	355m	955m	1510s	1020s	3010m	1435m	1040vs	822

s = strong, m = medium, vs = very strong

the bidentate nature of the dithiocarbamate ligand. The band at $\sim 950\text{ cm}^{-1}$ indicates the presence of W=O group in the complexes (Cousins *et al* 1964).

A number of skeletal vibrations appear around the 1000 cm^{-1} region due to the presence of cyclopentadienyl or indenyl groups. However these are quite weak compared to the $\nu(\text{C}\cdots\text{S})$ or $\nu(\text{W}=\text{O})$ stretching frequencies. Hence it is possible to distinguish these latter stretching frequencies even in the presence of skeletal vibrations due to organic ring systems. Further, the doublet observed in the unidentate behaviour of the dithiocarbamate moiety is a splitting of the band appearing at $\sim 1000\text{ cm}^{-1}$. Such splitting can be easily marked, even in the presence of other weak bands in the region. Thus IR spectral studies are a reliable criterion for determining the bonding mode of the dithiocarbamate ligand.

While assigning the co-ordination number to the cyclopentadienyl compounds, the latter group is assumed to occupy a single co-ordination site (Coutts *et al* 1970, 1974, 1975). Thus the compounds of the type $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{S}_2\text{CNR}_2)\text{Cl}$ [R = alkyl] (Kaushik *et al* 1978) and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{S}_2\text{CNHR})\text{Cl}$ [R = aryl] (Kaushik *et al* 1979) were assigned a co-ordination number five. Recently a co-ordination number six was assigned to the oxotungsten(VI) complexes of the type $(\eta^5\text{-C}_5\text{H}_5)_2\text{WO}(\text{S}_2\text{CNR}_2)\text{Cl}$ (Kaushik *et al* 1981). On this basis, the complexes reported in this paper may be assumed to be hexacoordinate.

All the complexes reported in this paper possess one band at $\sim 1500\text{ cm}^{-1}$ which reveals the thioureide band. As the frequency of this band lies between that of $\text{C}=\text{N}$ ($1350\text{--}1250\text{ cm}^{-1}$) and $\text{C}=\text{N}$ ($1690\text{--}1640\text{ cm}^{-1}$), this suggests that this bond possesses some double bond character.

The C-H stretching frequencies at $\sim 2990\text{--}3000\text{ cm}^{-1}$ in the complexes reported indicate indenyl and cyclopentadienyl group.

The band at $\sim 365\text{ cm}^{-1}$ indicates the presence of W-Cl group in the complexes, while that at $\sim 350\text{ cm}^{-1}$ is assigned to the tungsten-sulphur stretching frequency (Bradley *et al* 1969).

2. Electronic spectra

The electronic spectra of the complexes recorded in nujol, exhibited a single band in the range $24600\text{--}24200\text{ cm}^{-1}$ region which may be assigned to the charge transfer band (Dunn *et al* 1962) in accord with the electronic configuration $(n-1)d^0ns^0$ of tungsten in each case.

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A theoretical study on the specific interaction of hexafluorobenzene with benzene and *p*-xylene

D V S JAIN* and F S NANDEL

Department of Chemistry, Panjab University, Chandigarh 160 014, India

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Abstract. A CNDO/2 study has been carried out for $C_6F_6 + C_6H_6$ and $C_6F_6 + C_8H_{10}$ composites and individual molecules. The favoured configurations of the adducts have been decided on the basis of energy calculations of various geometries. For the $C_6F_6 + C_6H_6$ adduct the lowest energy corresponds to the configuration in which the molecular planes are parallel to each other with a twist angle of 30° . For the $C_6F_6 + C_8H_{10}$ adduct lowest energy corresponds to a geometry in which the two molecular planes are inclined by a small angle with the angle of twist between the molecular planes being 30° . It is shown that the complexes are not of the charge transfer type.

Keywords. CNDO study ; benzene ; hexafluorobenzene ; *p*-xylene ; charge transfer.

1. Introduction

The formation of complexes between hexafluorobenzene and alkyl benzenes is quite well-known (Patrick and Prosser 1960 ; Duncan *et al* 1966 ; Boeyens and Herbstein 1966). However, the nature of the specific interaction has not been well understood. It was earlier suggested (Patrick and Prosser 1960 ; Fenby *et al* 1966) that this has the nature of electron transfer interaction with benzene acting as donor and hexafluorobenzene as an acceptor. Thermodynamic studies on alkyl benzenes + hexafluorobenzene showed (Fenby and Scott 1967 ; Duncan *et al* 1966) that the excess enthalpy became more negative with the substitution of alkyl group in benzene. This was taken as an evidence for the charge transfer type of interaction because alkyl substitution also increased the electron donating power of the alkyl benzenes. However, no charge transfer bands were observed spectroscopically. As a matter of fact more recent (Gaw and Swinton 1968) thermodynamic studies and calculations based on quadrupole interactions (Broth and Swinton 1974) indicate that these interactions arise principally from electrostatic forces. Depolarised Rayleigh light scattering study (Brown *et al* 1978) gives indirect evidence for the existence of $C_6H_6 + C_6F_6$ adduct with their planes parallel to each other even in the liquid solutions. In the absence of any unequivocal experimental evidence we report the CNDO/2 calculations (Pople and

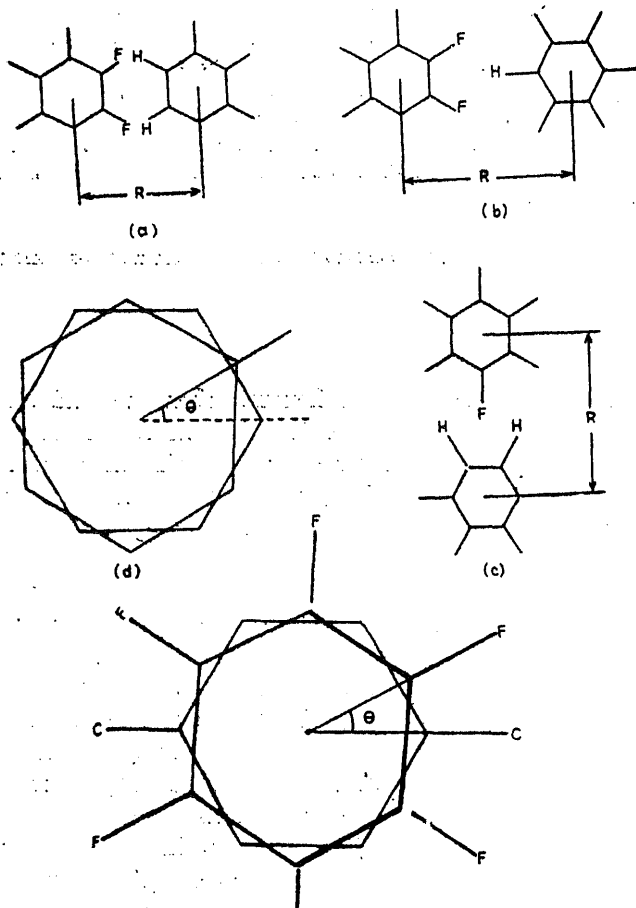
* To whom correspondence should be made.

Beveridge 1970) on the energies and charge distributions of the benzene (*p*-xylene) and hexafluorobenzene molecules separately and also for the composite molecules in which the distance between the centres of mass of C_6H_6 (C_6H_{10}) and C_6F_6 and their relative orientations have been varied.

2. Geometries

The following relative orientations (figure 1) of benzene (*p*-xylene) with respect to hexafluorobenzene in the complex have been considered:

(i) Those in which the benzene (*p*-xylene) and hexafluorobenzene molecules were in the same plane as shown in figures 1a and 1b.



(ii) Those in which the six-fold axis of benzene (*p*-xylene) lies in the molecular plane of hexafluorobenzene and one of the fluorine atom points towards the centre of the benzene molecule (figure 1c). For this configuration the HFB molecular plane has been rotated around the two-fold axis passing through the fluorine atom pointing towards benzene ring by 0 to 30°.

(iii) Those in which the molecules are placed one above the other and the twist angle between the molecular planes has been varied from 0 to 30° (figure 1d).

(iv) Those in which the molecular planes are inclined to each other (figure 1e). For symmetry consideration this was considered only for the hexafluorobenzene/*p*-xylene complex.

The energy of the molecular systems hexafluorobenzene and benzene (*p*-xylene) has been calculated as a function of the distance between the interacting molecules for all the above configurations. The molecular geometries of benzene (*p*-xylene) and hexafluorobenzene in the complex are assumed to be those of the isolated molecules ($R_{CC} = 1.397$ Å, $R_{CH} = 1.10$ Å, $R_{CF} = 1.37$ Å, and $R_{CC'} = 1.52$ Å). The intermolecular interaction energy (ΔE) is defined by the difference:

$\Delta E = \text{Energy of composite molecule} - \text{the sum of the energies of isolated molecules.}$

3. Results and discussion

The results obtained for the various configurations of different classes are summarised in tables 1 and 2. It is found that the configurations falling in categories (i) and (ii) have the least stabilization energy. The intermolecular distances for these configurations were also varied but only the distances corresponding to the lowest energy is recorded for these geometries. Configurations with $\theta = 30^\circ$ were found to be the most stable from category (iii) for benzene + hexafluorobenzene complex. A plot of ΔE vs. R for this is shown in figure 2 which shows a

Table 1. CNDO stabilization energy for the benzene-hexafluorobenzene adduct as a function of distance (R) and geometry.

Geometry	θ/degree	$R/\text{\AA}$	$-\Delta E \times 10^3/\text{a.u.}$
I	(a)	7.30	0.576
	(b)	5.50	0.400
II	0	3.00	5.400
	15	3.00	5.372
	30	3.00	0.123
III	0	3.00	0.654
	15	3.00	5.911

Table 2. Stabilization energy $-\Delta E \times 10_3$ for *p*-xylene-hexafluorobenzene system at various tilt angles (ϕ) between the molecular planes [twist angle (θ) being 30°].

$d/\text{\AA}$	ϕ			
	0°	4°	6°	8°
2.60		2.315		
2.70		2.860	3.215	
2.80	2.396	2.843	3.168	3.046
2.90		2.555	2.803	3.625
3.00	1.910	2.163	2.317	
3.10		1.759		

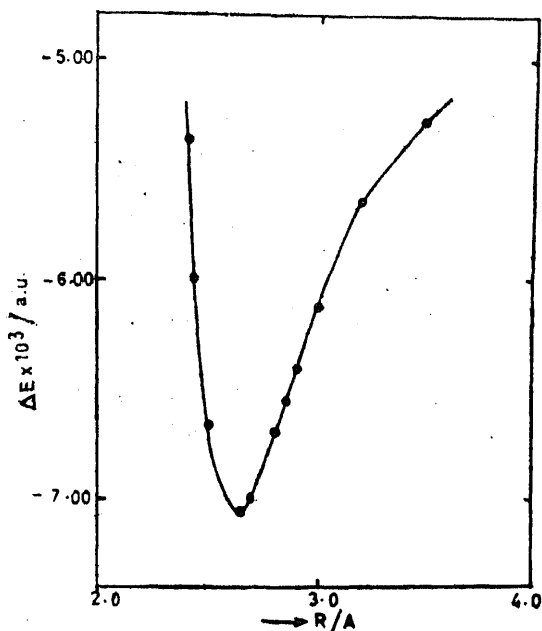
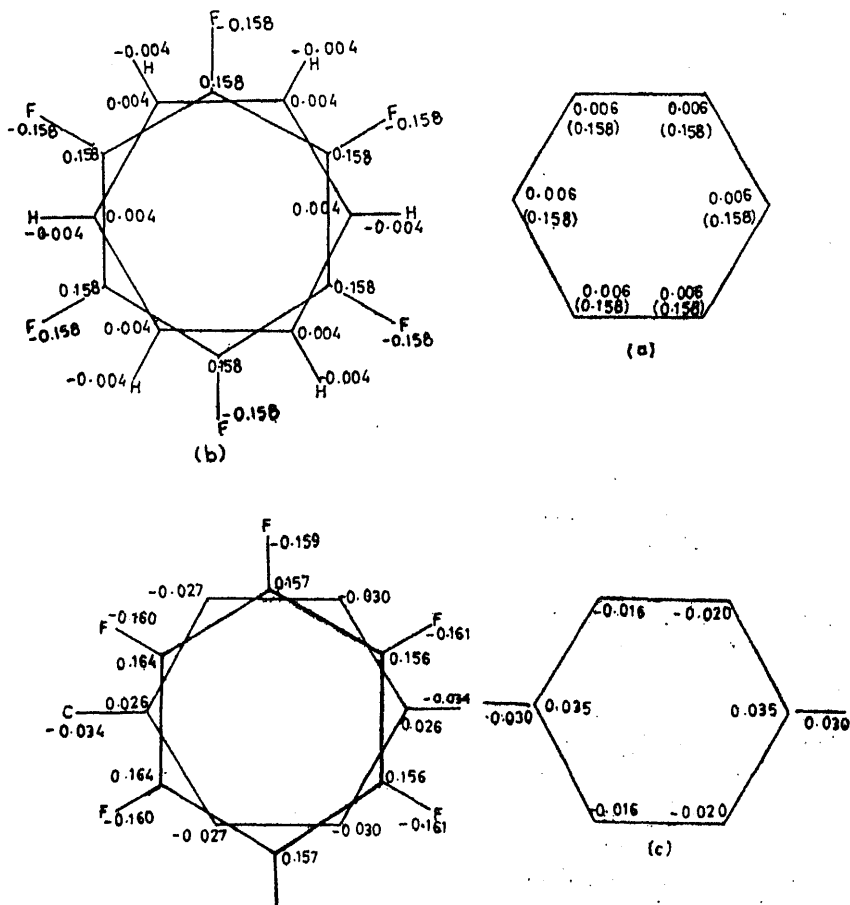


Figure 2. CNDO stabilization energies for benzene-hexafluorobenzene as a function of distance between the two molecules.

minimum at $R = 2.65 \text{ \AA}$. Crystallographic studies (Dahl 1972, 1975) on some of the alkyl benzenes and hexafluorobenzene adducts also indicate that these

for HFB-*p*-xylene complex, the most stable geometry is that in which the molecular planes of both the molecules are twisted by 30° and are inclined by a small angle ϕ (figure 1e). It was found that the maximum stabilization takes place at $\phi \simeq 6^\circ$ (table 2). This is consistent with the crystallographic studies (Dahl 1975) in which the inclination angle of 5.4° is reported.

The charges on various atoms in the isolated molecules and in the composite molecules for stabilized geometries are given in figure 3. It can be seen that there is very little intermolecular charge transfer. There is only intramolecular adjustment of charges on atoms on each molecule. It is also apparent from the HOMO and LUMO of the molecules (figure 4) that the charge transfer from benzene (*p*-xylene) to hexafluorobenzene is not energetically favoured.



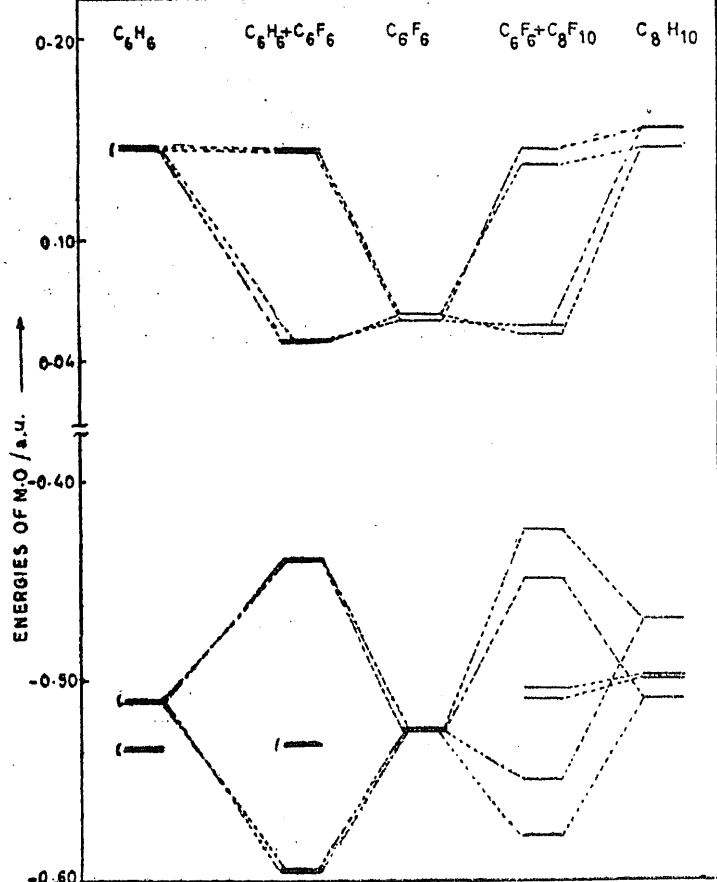


Figure 4. Energies of HOMO and LUMO of benzene (*p*-xylene) and hexafluorobenzene and their adducts.

We have carried out the correlation of the molecular orbitals of the composite molecule with the molecular orbitals of the individual hexafluorobenzene and benzene (*p*-xylene) molecules. It is evident from figure 4 that the interaction of highest occupied molecular orbitals play insignificant role in stabilization. Actually this leads to slight destabilization. It was noted for both the complexes that the stability arises due to the interaction of some lower molecular orbitals.

The theoretical calculations agree with the crystallographic studies regarding the configuration of the complexes. The calculated intermolecular distances are small. This, however, is a general weakness of CNDO method. Our calculations also explain the results of depolarized Rayleigh scattering study of benzene+hexafluorobenzene system.

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Conformational behaviour and vibrational spectra of 3-methyl 2-butanethiol

S K NANDY and G S KASTHA*

Department of Physics, Jadavpur University, Calcutta 700 032, India

* Optics Department, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India

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Abstract. The Raman spectra of 3-methyl 2-butanethiol in the temperature range -120°C to $+60^{\circ}\text{C}$ have been recorded together with its liquid phase infrared spectrum at room temperature. The spectral analysis shows that the molecule of the compound exists in the liquid state, in three different rotameric configurations *A*, *B* and *C* of which the form *A* is the stablest. Besides, a tentative assignment of the observed vibrational frequencies arising from the rotameric forms has been presented.

Keywords. Raman spectra; infrared spectra; temperature dependence of Raman band intensities; rotational conformers; energy differences; vibrational experiment.

1. Introduction

Rotational isomerism in substituted alkanes has been studied both experimentally and theoretically. It is now fairly well understood how the different rotameric properties, such as the number of stable rotational conformers, their stabilities and energy differences in these molecules change with the nature, position and number of substituents specially, when the substituents are halogen atoms. However, this is not so if the substituent is a group of atoms like the thiol group. Experimental data on rotational isomerism in alkane thiols and theoretical computations (Freeman 1974) are meagre and far from adequate. Nevertheless, it has been possible to interpret the experimental data by assuming that the rotational conformers in mercaptoalkanes arise mainly due to rotations about the skeletal C-C bonds and that the thiol group remains oriented in a fixed configuration except in the rare case of ethyl mercaptan (Smith *et al* 1968 ; Wilson 1972). But the task of ascertaining how the number of stable rotational isomers and their stabilities depend on the position of the substituent thiol group requires the acquisition of more experimental data in differently-substituted alkanethiols. Accordingly detailed Raman spectroscopic investigations on the vibrational spectrum of 3-methyl 2-butanethiol in the temperature range -120°C to $+60^{\circ}\text{C}$ and the IR spectrum of the same compound in the liquid phase has been studied.

*To whom correspondence should be made.

alkanethiols including the two very similar molecules of 2-methyl-1-propanethiol (Ozaki *et al* 1975) and 2-butanethiol (McCullough *et al* 1958). These experimental data together with their discussion form the subject-matter of this paper.

2. Experimental

3-methyl 2-butanethiol from M/s. Schuardt (Germany) was distilled under reduced pressure and its Raman spectrum in the liquid state was obtained both photographically and with a 200 mW 4880 Å radiation of argon ion laser source of a Cary 82 and Spex C laser Raman spectrophotometers. The Raman spectrum in the solid state, the polarisation character of the Raman lines and the temperature dependence of the intensities of some of the Raman lines in the range -120°C to 60°C were studied with the same spectrophotometers. The IR spectrum was recorded in a Perkin Elmer model 21 spectrophotometer with rock salt optics.

3. Results

The Raman and IR frequencies with estimated relative intensities in different phases are given in table 1. The polarisation character of the Raman lines are also shown in the table including the probable assignments of the observed frequencies in terms of the modes of vibration in different rotameric forms of the molecule. The variation in the intensities of Raman lines due to C-S stretching mode of vibration at three temperatures is shown in figure 3.

4. Discussions

4.1. Rotameric forms and their stabilities

If the CH_3 groups are considered rigid and the SH group given a fixed orientation the molecule of 3-methyl 2-butanethiol will have only one central C-C axis of rotation. The three rotational conformers arising due to orientation about this bond are shown in figure 1 and are indicated as *A*, *B* and *C*. It may be noted that while in form *C*, the thiol group is in the trans-position with respect to the hydrogen atom, in forms *A* and *B* they are gauche with respect to each other.

The configuration of these rotamers is very similar to that obtained in 2-butanethiol in which there is a H-atom in place of one of the two CH_3 groups in the second carbon atom. These forms shown in figure 2 have energies, according to McCullough *et al* (1958), in the order $E_C > E_B \geq E_A$. From a comparison of these three rotameric forms with those of 3-methyl 2-butanethiol and considerations of the nonbonded interactions in the various groups in the different conformers of the two molecules the energies of the three conformers of 3-methyl 2-butanethiol are found to be $E_B > E_C > E_A$ in the free state. The three rotamers will have approximately the same dipole moment and lowering of energy in the liquid phase is not expected to change the relative energy differences significantly. In other words, the form *A* will be the most stable and with lowering of temperature, the

IR bands (cm ⁻¹) liquid (thin film)	Raman shifts (cm ⁻¹)		Assignment	Rotamer
	Liquid	Glassy mass (-120° C)		
	109 (3)		C-C torsion	
	133 (1)		C-C torsion	
	225 (4) D	absent	C-C-S deformation	B/C
	320 (3) D	320 (2)	C-C-S deformation	A
	358 (5) P	absent	C-C-C deformation	B
	425 (5) P	425 (2)	C-C-C deformation	B/C
	483 (6) P	483 (3)	C-C-C deformation	B/C
	513 (4) P	513 (5)	C-C-C deformation	A
	623 (5) P	623 (8)	C-S stretch	A
	650 (10) P	650 (6)	C-S stretch	C
	680 (8) P	680 (5)	C-S stretch	B
780 (w)	786 (6) D	786 (10)	CSH angle deformation	A
870 (w)	872 (3) P	872 (3)	CSH angle deformation	B/C
900 (w)	915 (5) P	915 (4)	CH ₃ rock	B
960 (w)	960 (3) D	960 (3)	CH ₃ rock	C
	990 (3) D	990 (4)	C-C stretch/CH ₃ rock,	A
1015 (m)	1015 (1) P	absent	C-C stretch	B/C
	1030 (2) D	1030 (4)	C-C stretch	A
1080 (m)	1080 (3) P	1080 (2)	C-C stretch/CH ₃ rock	B/C
1110 (w)	1115 (3) D	1115 (4)	CH ₃ Rock	A
1150 (m)	1152 (3) D	1152 (5)	C-C stretch	A
	1188 (3) P	1188 (5)	C-C stretch	A
1235 (m)	1237 (5) P	1237 (4)	CH deformation	B/C
	1260 (2) D	1260 (4)	CH deformation	A
	1290 (3) P	1290 (3)	CH deformation	B/C
1330 (m)	1326 (3) D	1326 (5)	CH wagg	A
	1343 (2) D	1343 (2)	CH wagg	B/C
1360 (ssh)				
1370 (s)	1368 (1) P	1368 (2)	(CH ₃) bend sym.	
1390 (ssh)	1388 (2) P	1388 (2)		
1455 (vs)	1454 (8) D	1454 (8)	(CH ₃) def. asym.	
	1472 (7) D	1472 (8)		
2570 (m)	2569 (9) P	2569 (9)	(S-H) stretch	
2880 (s)	2860 (10) P	2860 (10)	(CH) ₂ of CH ₃ stretch	
2930 (ssh)	2910 (10) P	2910 (10)	(CH) of CH stretch	
2960 (vs)	2958 (5) D	2958 (9)	(CH) ₂ of CH ₃ stretch	

P, polarised ; D, depolarised ; s, strong ; m, medium ; w, weak ; v, very ; sh, shoulder.

It is seen from table 1 that there are three polarised Raman bands at 623, 650 and 680 cm^{-1} in the spectrum of 3-methyl 2-butanethiol. They correspond to the three frequencies 620, 659 and 684 cm^{-1} in 2-butanethiol which have been assigned to the C-S stretching vibrations in the three rotamers of the molecule by McCullough *et al* (1958). The former three Raman bands, by analogy, represent the ν (C-S) frequencies in the three rotamers of the present molecule. It is seen from figure 3 that the relative intensities of the three bands vary with change of temperature and this change is the largest for the band at 623 cm^{-1} . The intensity of this band increases appreciably with lowering of temperature and therefore, it is attributed to the most stable rotamer (A) of the molecule. The observed variation in the intensities of the Raman bands 650 and 680 cm^{-1} suggest their origin to forms C and B respectively. From plots of the variation of $\log I_{623}/I_{650}$ and $\log I_{623}/I_{680}$ against reciprocal of absolute temperature (figures 4, 5) the energy differences ΔE are obtained as 0.25 and 0.49 kcal/mol. It is seen that form C is more stable than form B by 250 cal/mol. This reasonably confirms the existence of three rotameric forms as assumed in the very beginning.

4.2. Assignment of the vibrational frequencies

4.2a. *Group vibrations*: The molecule of 3-methyl 2-butanethiol with 18 atoms will have 48 modes of vibration and 48 vibration frequencies. These may be classified roughly in terms of vibrations of the methyl groups, the C-H group, the CSH group and skeletal modes. To each of the three methyl groups, there belongs three C-H stretchings, three CH deformations, two CH_3 rocking and one $\text{H}_3\text{C}-\text{C}$ torsional modes of vibrations. The CH group will give rise to on

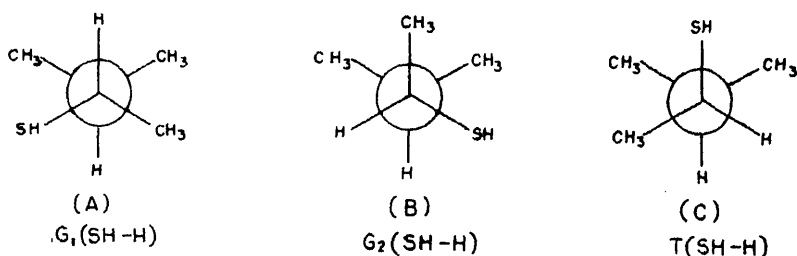


Figure 1. Three rotational conformers in 3-methyl 2-butanethiol.

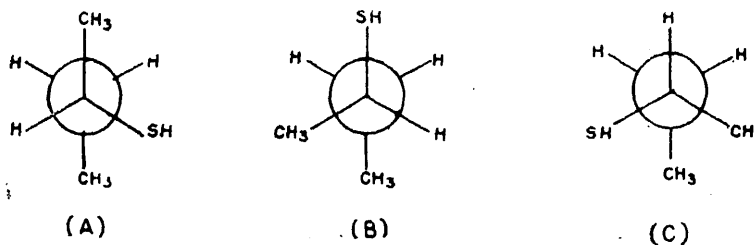


Figure 2. Three possible isomers in 2-butanethiol.

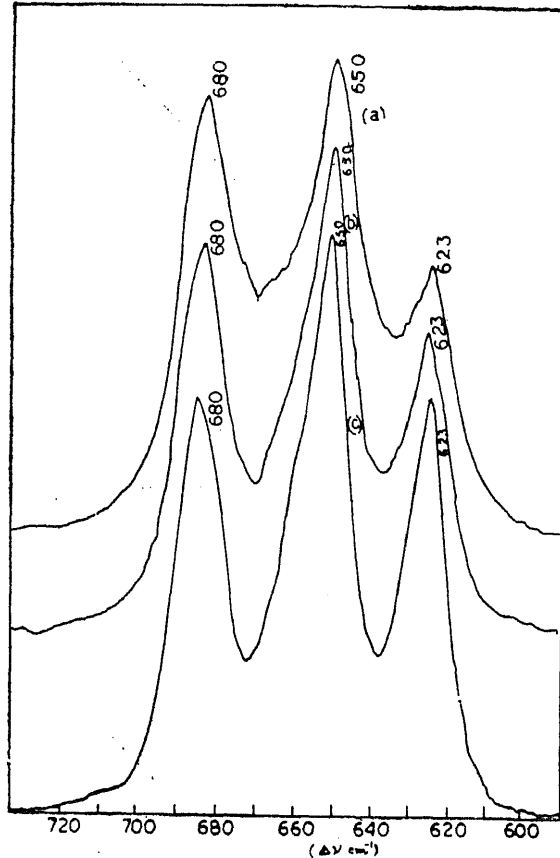


Figure 3. Variations in the intensities of Raman lines due to C-S stretching modes of vibration of 3-methyl, 2-butanethiol. (a) 333 K, (b) 260.5 K, (c) 213 K.

CH stretching and two CH deformation modes while there will be one S-H stretching vibration, one CSH angle deformation and one CS torsional mode for the SH group. The assignment of most of these modes is straightforward and is not given here. However, it is difficult to assign the vibrations arising from the torsional modes. Further, difficulties are experienced in separating the CH_3 rocking modes from those arising from C-C skeletal stretching vibrations. These are considered in the next section.

4.2b. *Skeletal vibrations*: The skeletal of 3-methyl 2-butanethiol molecules gives rise to 12 vibrational frequencies in each rotamer and they may be broadly classified as C-C torsion (1), C-C-S deformations (2), C-C-C deformations (3), C-C stretching (4), and C-S stretching (1). All these vibrations are sensitive to the configuration of the rotamers. Some of their assignments are discussed below.

The two low frequency Raman bands 109 and 133 cm^{-1} observed in the Raman spectrum of the liquid at room temperature are believed to arise from torsional vibrations, but their assignments are not definite. In most monomeric alkanes there

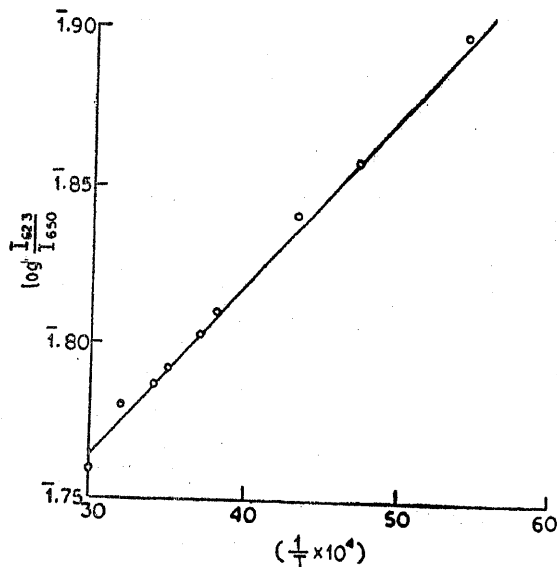


Figure 4. Plot of $\log I_{623}/I_{650}$ vs. $1/T$.

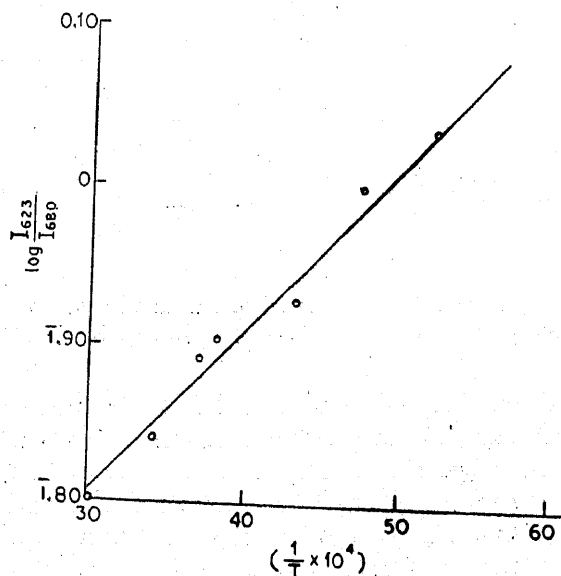
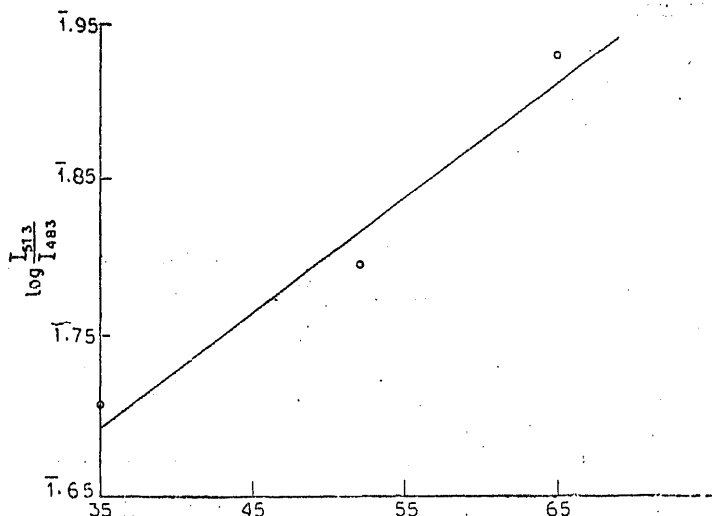


Figure 5. Plot of $\log I_{623}/I_{680}$ vs. $1/T$.

C-C-S deformation vibration. In the present molecule, the two frequencies 225 and 320 cm^{-1} most probably represent this mode of vibration. Since with lowering of temperature, the former vanishes and there is little change of intensity in the latter, the frequency 225 cm^{-1} corresponds to the least stable of the forms *B* and *C* while the latter represents one of the two δ (C-C-S) modes due to form *A*.

Accordingly the polarised Raman bands 358, 425, 483 and 513 cm^{-1} observed in the liquid phase spectrum of 3-methyl 2-butanethiol are assigned to this mode of vibration. It may be noted that these bands strikingly correspond to the frequencies 377, 412, 453 and 517 cm^{-1} assigned to $\delta(\text{C}-\text{C}-\text{C})$ mode in 2-butanethiol by McCullough *et al* (1958). The first of these bands vanishes at low temperature and should be attributed to the least stable form, the other two bands whose intensities decrease appreciably on cooling should correspond to the forms *B* or *C*. The intensity of the band 513 cm^{-1} , on the other hand, slightly increases at low temperature and thus is attributed to form *A*. Though not all the possible twelve frequencies due to $\delta(\text{C}-\text{C}-\text{C})$ modes in the rotamers have been recorded, the presence of Raman bands whose intensities vary differently with lowering of temperature confirms the presence of at least two rotamers. From a plot of $\log I_{513}/I_{483}$ against $1/T$ (figure 6) the energy difference between the conformers *A* and *B* or *C* or both, is obtained as 0.34 kcal/mol, which is roughly the average of the energy difference values between (i) forms *A* and *B*, and (ii) forms *A* and *C*, obtained from the temperature dependence of Raman bands due to C-S stretching modes of vibration.

The frequencies due to C-S stretching vibrations have already been discussed and those due to C-C skeletal stretching are now considered. As with the $\delta(\text{C}-\text{C}-\text{C})$ modes, in this case also we should expect twelve C-C stretching vibrations appropriate to the three rotamers. From the data obtained from published literature, the Raman bands in the frequency region 900–1200 cm^{-1} are believed to arise from C-C stretching modes. However, where there are methyl groups in the molecule, the two CH_3 -rocking modes appear respectively in the region 850–1000 cm^{-1} and at about 1100 cm^{-1} , which makes reliable assignment of the $\nu(\text{C}-\text{C})$ frequencies difficult. The frequencies 915, 960, 990, 1015, 1030, 1080, 1115, 1152 and 1183 cm^{-1} observed in the vibration spectra of 3-methyl 2-butanethiol certainly represent the two CH_3 -rocking modes and C-C stretching modes of



vibrations in the three rotamers. Of these 1152 and 1183 cm^{-1} definitely belong to ν (C-C) mode and since their intensity increases when the temperature is lowered they are associated with the rotamer *A*. From a comparison with the ν (C-C) frequencies observed in 1,2,ethanedithiol 1, 3 propanedithiol and 2-mercapto-ethanol (Hayashi *et al* 1965 ; Nandy *et al* 1973a, b ; Som *et al* 1975) where there are no complications arising from CH_3 rocking modes of vibration, the Raman bands 1015 and 1030 cm^{-1} are assigned to the ν (C-C) vibrations, the former belonging to the less stable forms *B* or *C* and the latter to form *A*. In view of the CH_3 rocking frequencies proposed for 2-methyl 1-propanethiol (Ozaki *et al* 1975; Scott *et al* 1958) and 2-butanethiol (McCullough *et al* 1958), the bands 915, 960 and 1115 cm^{-1} may be reasonably assigned to this mode in the three rotamers as shown in table 1. The two Raman bands 990 and 1080 cm^{-1} may arise from either R (CH_3) or ν (C-C) modes but their assignment is not certain.

Some comments on the C-S-H deformation frequencies of 3-methyl 2-butanethiol are in order. In different alkanethiols the frequencies corresponding to these modes have variously been put in the frequency interval 775 to 900 cm^{-1} . For example Ozaki *et al* (1975) has assigned the Raman band at 774 cm^{-1} in 2 methyl 1-propanethiol to δ (C-S-H) modes while Torgrimsen and Klæboe (1970) has proposed for this mode two Raman frequencies 778 and 814 cm^{-1} in 1-propanethiol. In 1-2 ethanedithiol (Hayashi *et al* 1965), the two modes are at 800 and 890 cm^{-1} and McCullough *et al* (1958) have attributed the frequency 863 cm^{-1} to the δ (C-S-H) mode in 2-butanethiol. Following these observations the two Raman frequencies 786 and 872 cm^{-1} observed with the present molecule are assigned to the CSH angle deformation mode. Since the intensity of 786 cm^{-1} Raman band increases at low temperature it certainly originates from the most stable *A* rotamer.

Acknowledgements

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Determination of ionisation constants of nitrobenzidines

S ARAVAMUTHAN, C KALIDAS and C S VENKATACHALAM*

Department of Chemistry, Indian Institute of Technology, Madras 600036, India

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Abstract. The ionisation constants of 2-nitrobenzidine, 2,2'-dinitrobenzidine and 2,3'-dinitrobenzidine were determined spectrophotometrically in 33.3% (w/w) methanol. The low pK value obtained for 2,3'-dinitrobenzidine when compared to that of 2-nitro and 2,2'-dinitrobenzidines is explained on the basis of electron withdrawing nature of the nitrogroup and intramolecular hydrogen bonding.

Keywords. Ionisation constant ; spectrophotometry ; nitrobenzidines.

1. Introduction

Nitrobenzidines particularly, 2-nitrobenzidine (2-NB) and 2, 2'-dinitrobenzidine (2, 2'-DNB) have considerable importance in the preparation of azo-dyes (Kuhn 1959) and polycyclic cinnoline derivatives (Braith Waite *et al* 1958). It is well-known that organic electrode processes are pH dependent (Kolthoff and Lingane 1952) and in order to study the variation of polarographic half-wave potential ($E_{1/2}$) of an electro-active material (depolariser) with the pH of the medium, the determination of ionisation constant (pK) of the depolariser becomes necessary. The importance of pK determination towards the elucidation of electro-reduction of organic compounds is well-known (Holubek and Volke 1962; Laviron 1962). Hence, in this paper we describe a spectrophotometric method for the determination of ionisation constants of 2-NB, 2, 2'-DNB and 2, 3'-dinitrobenzidine (2, 3'-DNB) in methanol-water mixtures. It may be pointed out that pK values for these nitrobenzidines have not been reported earlier.

2. Experimental

2-Nitrobenzidine (4,4'-diamino-2-nitro biphenyl, Kovar 1964), 2,2'-dinitrobenzidine (4,4'-diamino-2,2'-dinitro biphenyl, Porai *et al* 1945) and 2,3'-dinitrobenzidine (4,4'-diamino-2,3'-dinitro biphenyl, Lefevre and Turner 1926) were prepared according to the literature procedure. Their purity was checked by

infrared spectra and mass spectrometry. Methanol was purified by the standard procedure before use.

The ionisation constants of 2-NB, 2,2'-DNB and 2,3'-DNB were determined by a spectrophotometric method in 33.3% (w/w) which corresponds to 40% (v/v) methanol-water mixtures (Chattanathan 1971). Solutions of different pH values were prepared in 33.3% (w/w) methanol-water mixture according to the procedure given by Bates *et al* (1963). Solutions of lower pH values were prepared from perchloric acid of different molalities. The pH of various solutions were measured using a KNICK precision pH meter (accuracy ± 0.01 pH unit). The ultraviolet absorption data were obtained with a Carl-Zeiss (ZFM4) spectrophotometer for a definite concentration of each of the nitrobenzidines at different pH values. In the case of 2,3'-DNB, the pK determination was carried out in perchloric acid of different molalities since it was found that no appreciable change in the absorption was noticed for 2,3'-DNB in the pH range 0.4-2.3.

3. Results and discussion

The ionisation constant (pK_{BH^+}) of a base (B) for the equilibrium $BH^+ \rightleftharpoons B + H^+$ can be calculated from the relation (Bates *et al* 1963),

$$pK'_{BH^+} = \log(C_{BH^+}/C_B) - \log C_{H^+}, \quad (1)$$

where the apparent ionisation constants, pK'_{BH^+} tends to pK_{BH^+} as the molar concentration of the acid in the solvent tends to zero. In the present work, the ionisation ratios (C_{BH^+}/C_B) of various nitrobenzidines were measured spectrophotometrically. Using these and the equilibrium concentration of H^+ ions, the apparent ionisation constants (pK'_{BH^+}) for 2-NB, 2,2'-DNB and 2,3'-DNB were calculated from equation (1). pK_{BH^+} for the nitrobenzidines were obtained by plotting pK' against the acid concentration and extrapolating the linear plot to infinite dilution. A typical plot is shown in figure 1. The spectral data are presented in

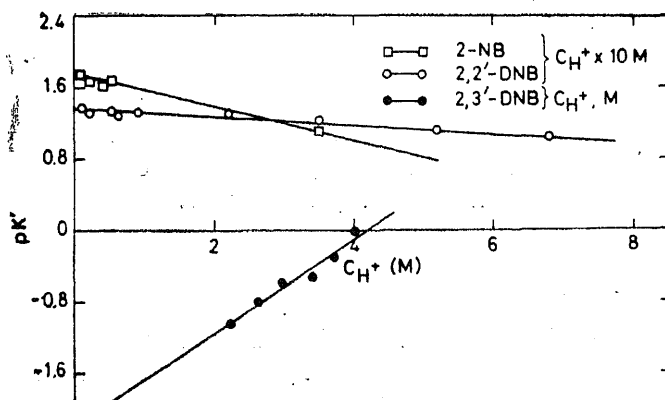


table 1. The pK_{BH^+} values obtained from such a plot for 2-NB, 2,2'-DNB and 2,3'-DNB at the wavelength where the ionisation ratios (C_{BH^+}/C_B) between the protonated and unprotonated nitrobenzidines exhibit a large difference ($\lambda = 400$ nm in all the cases) were 1.76 ± 0.02 , 1.34 ± 0.04 and -2.10 ± 0.04 , respectively. It may be pointed out that pK_{BH^+} values calculated at other wavelengths corresponding to $\lambda = 380$ and 390 nm for 2-NB and 2,2'-DNB and $\lambda = 410$ and 430 nm for 2,3'-DNB were found to be independent of the wavelength within the limits of experimental error.

Table 1. Absorbance (D) and molar extinction coefficients (ϵ) for nitrobenzidines at the wavelength ($\lambda = 400$ nm) at various pH values in 33.3% (w/w) methanol-water mixtures. Temperature $30 \pm 0.1^\circ \text{C}$.

Substance	pH	D	ϵ	C_{BH^+}/C_B	pK'
2-nitrobenzidine ($6.0 \times 10^{-4} \text{ M}$)					
	0.45	0.120	200	4.92	1.14
	0.83	0.155	258	...	...
	1.32	0.205	342	2.22	1.67
	1.45	0.275	458	1.34	1.58
	1.71	0.335	558	0.90	1.66
	1.93	0.380	633	0.66	1.75
	2.11	0.490	817	...	...
2,2'-dinitrobenzidine ($3.0 \times 10^{-4} \text{ M}$)					
	0.17	0.11	367	9.83	1.16
	0.28	0.13	433	7.13	1.14
	0.45	0.14	467	6.22	1.25
	0.65	0.17	550	4.65	1.32
	1.04	0.28	917	1.88	1.32
	1.22	0.35	1167	1.17	1.29
	1.45	0.44	1467	0.67	1.27
	1.92	0.56	1867	0.27	1.36
	2.26	0.63	2100	0.12	1.34
2,3'-dinitrobenzidine ($2.0 \times 10^{-4} \text{ M}$)					
	-0.61	0.31	1550	3.81	-0.03
	-0.57	0.42	2100	1.85	-0.30
	-0.53	0.53	2650	1.03	-0.52
	-0.47	0.62	3100	0.75	-0.60
	-0.41	0.70	3500	0.40	-0.81
	-0.35	0.79	3950	0.20	-1.04

The low pK_{BH^+} values obtained for nitrobenzidines when compared to benzidine (Albert and Serjeant 1971) may be attributed to the electron withdrawing tendency of the nitro group. The low pK_{BH^+} values of 2,2'-DNB in comparison with 2-NB indicates that 2,2'-DNB is less basic than 2-NB due to the presence of additional nitro group in the molecule. The negative value of pK_{BH^+} obtained for 2,3'-DNB (-2.10 ± 0.04) may be explained on the basis of the fact that the presence of one of the nitro-groups either in 3 or 3' position would decrease the basic character of the compound due to intramolecular hydrogen bonding with the amino group in 4 or 4' position of the biphenyl ring.

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Equilibria in the system containing chloride and sulphates of potassium and magnesium

V R K S SUSARLA* and K SESHADRI

Central Salt and Marine Chemicals Research Institute, Bhavnagar 364 002, India

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Abstract. Reciprocal salt-pair system $2\text{KCl} + \text{MgSO}_4 \rightleftharpoons \text{K}_2\text{SO}_4 + \text{MgCl}_2$ has been studied at 35°C to eliminate the discrepancies reported by different workers and for correlating the experimental data with natural evaporation of brine (without NaCl) so as to recover potash salts.

Keywords. Schoenite ; leonite ; kainite ; kieserite.

1. Introduction

The various processes employed for the production of potassium salts from sea water concentrates depend upon the equilibria existing in the reciprocal salt-pair system $2\text{KCl} + \text{MgSO}_4 \rightleftharpoons \text{K}_2\text{SO}_4 + \text{MgCl}_2$ at the desired temperature. Van't Hoff (1918) studied the system at 25°C and 83°C and pointed out the existence of leonite and kainite at 25°C , but the boundaries of these salts were not clear. Autenrieth (1954) studied both stable and metastable equilibria to establish the transition from schoenite to leonite. Further work was carried out by D'Ans (1933) and Campbell (1934) at other temperatures such as at 0°C , 55°C and 100°C . Campbell did not report the existence of kainite at 100°C , but Van't Hoff pointed out its existence at 83°C . When the above data were used to interpret the extraction process of potassium and magnesium salts from brine and bittern, considerable variations were observed.

In tropical countries like India, bittern gets evaporated between 30° to 45°C and therefore an understanding of the above system is necessary. To establish the various equilibria the above reciprocal salt-pair system has been studied at 35°C .

2. Experimental methods

For studying the reciprocal salt-pair system at 35°C , a constant temperature water bath maintained at the above temperature was used. For establishing the time for various equilibrium stages, the contents of the system were allowed to stir

* To whom correspondence should be made.

of the two successive results only further progress was made in studying the system.

The common methods of analysis such as magnesium by EDTA, chloride by Mohr's method, potassium by tetraphenylborate, sulphate by gravimetric estimation of BaSO_4 were used. The EEL flamephotometer was used to check the analysis of potassium by the above method.

In the preliminary stages the equilibria in the various connected binary systems were obtained. The compositions of various binary solutions of the salts—potassium chloride, magnesium chloride hexahydrate, magnesium sulphate heptahydrate and potassium sulphate were noted. A saturated solution of one salt was then added to a second solid salt having a common ion to get the invariant point as represented by the composition of the solution where the solid in contact with the solution showed the presence of both the salts. In the more complicated system, the third salt was added to a system where the solution was in equilibrium with two salts. This gave the various invariant points on the diagram with respect to the solid phase with which three salts were in equilibrium. The various fields or boundaries were established for the double salts—schoenite, leonite, kainite, kieserite etc.

In all the above cases the solid phase compositions have been obtained by chemical methods of analysis and were confirmed by using x-ray diffraction and differential thermal methods of analysis (DTA). This enabled checking and establishing the nature of various equilibria in the system and information about the nature of the solid phase at each stage.

3. Results and discussion

The above system, *i.e.*, $2\text{KCl} + \text{MgSO}_4 \rightleftharpoons \text{K}_2\text{SO}_4 + \text{MgCl}_2$ at 35°C formed a reciprocal salt-pair. The analytical results obtained are given in table 1 and diagrammatically shown in figures 1 and 2 by Löwenherz's and Jänecke's method of projection. In figure 1 the horizontal axis was used to represent 2KCl (or K_2Cl_2) and MgSO_4 and the vertical ordinate to represent K_2SO_4 and MgCl_2 and the results were expressed in moles/1000 moles of water. In Jänecke's method of projection (figure 2) the compositions of the solutions were expressed in mole per cent of the dissolved salts. The composition of various solutions occurring at different invariant points is given in alphabetical order of names.

3.1. Critical points consisting of one or two salts with a common ion

In all the points A, B, C and D where KCl , K_2SO_4 , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ are in equilibrium, the results fairly agree with previous data (Autenrieth 1954). The same is true for the points E, F, G, H, I, J, K and L where the solutions were saturated with respect to the salts having a common ion.

3.2. Critical points representing solutions in equilibrium with three salts

As mentioned above, all the points have been obtained by starting the experiments with a solution saturated with respect to two salts. Starting from point

Table 1. Solubility data in the system $2\text{KCl} + \text{MgSO}_4 \rightleftharpoons \text{K}_2\text{SO}_4 + \text{MgCl}_2$ at 35°C

	Composition of the liquid phase										Solid Phase
	in moles/1060 moles of H ₂ O					in mole % of the dissolved salts					
	K ₂ Cl ₂	MgCl ₂	K ₂ SO ₄	MgSO ₄	K ₂ Cl ₂	MgCl ₂	K ₂ SO ₄	MgSO ₄			
	1	2	3	4	5	6	7	8	9		
A	46.86	..	..	..	100.0	..	..	..	KCl		
B	..	..	15.32	..	..	..	100.00	..	K ₂ SO ₄		
C	..	..	..	59.26	..	100.00	..	..	MgSO ₄ 7H ₂ O		
D	..	108.2	..	..	..	..	..	100.00	MgCl ₂ 6H ₂ O		
E	6.15	73.18	..	..	7.75	92.25	..	..	KC + Carnallite		
F	0.39	106.10	..	..	0.36	99.64	..	..	Carnallite + MgCl ₂ - 6H ₂ O		
G	45.83	..	1.64	..	96.46	..	3.54	..	KCl + K ₂ SO ₄		
H	..	72.97	..	11.35	..	86.54	..	13.46	MgSO ₄ 7H ₂ O + MgSO ₄ 6H ₂ O		
I	..	103.61	..	8.05	..	92.79	..	7.21	MgSO ₄ 6H ₂ O + MgSO ₄ H ₂ O		
J	..	103.66	..	4.92	..	95.47	..	4.53	MgSO ₄ H ₂ O + MgCl ₂ 6H ₂ O		
K	..	..	17.29	27.45	..	..	38.65	61.37	K ₂ SO ₄ + Schoenite		
L	..	..	6.91	62.91	..	..	9.94	90.07	Schoenite + MgSO ₄ 7H ₂ O		
M	15.24	25.33	..	14.84	27.50	45.71	..	26.78	K ₂ SO ₄ + Schoenite + Leonite		
N	10.57	47.25	..	15.07	14.50	64.82	..	20.67	KCl + Leonite + Schoenite + Kainite		
O	5.39	71.3	..	5.27	6.58	86.99	..	6.43	KCl + Carnallite + Kainite		
P	8.03	48.00	..	17.53	11.16	65.10	..	23.78	Kainite + MgSO ₄ 7H ₂ O + Schoenite		
Q	4.54	67.50	..	11.83	5.41	80.48	..	14.11	MgSO ₄ 6H ₂ O + MgSO ₄ 7H ₂ O		
R	0.53	74.99	..	9.19	0.63	88.53	..	10.65	Kainite		
S	1.34	99.95	..	6.79	1.24	92.48	..	6.28	MgSO ₄ 6H ₂ O + Kainite + Kieserite + Carnallite		
T	16.37	32.24	..	13.16	29.1	57.5	..	23.4	Carnallite + Kieserite + MgSO ₄ 6H ₂ O		
							..		KCl + K ₂ SO ₄ + leonite		

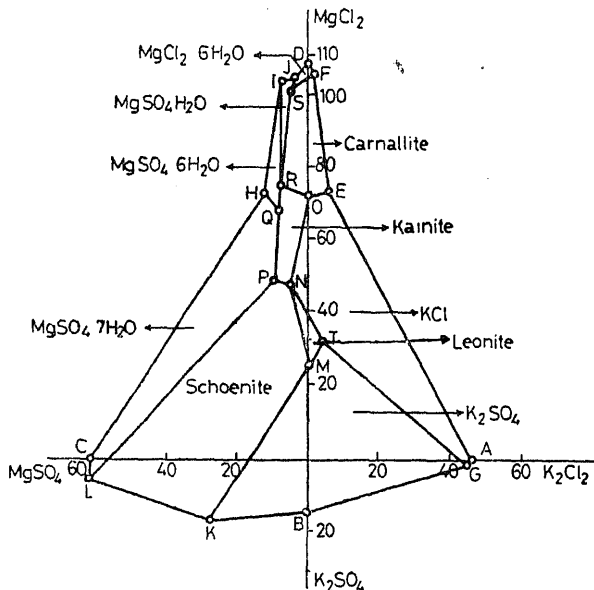


Figure 1. Study of the system $2\text{KCl} + \text{MgSO}_4 \rightleftharpoons \text{K}_2\text{SO}_4 + \text{MgCl}_2$ at 35°C (Löwenherz's method)

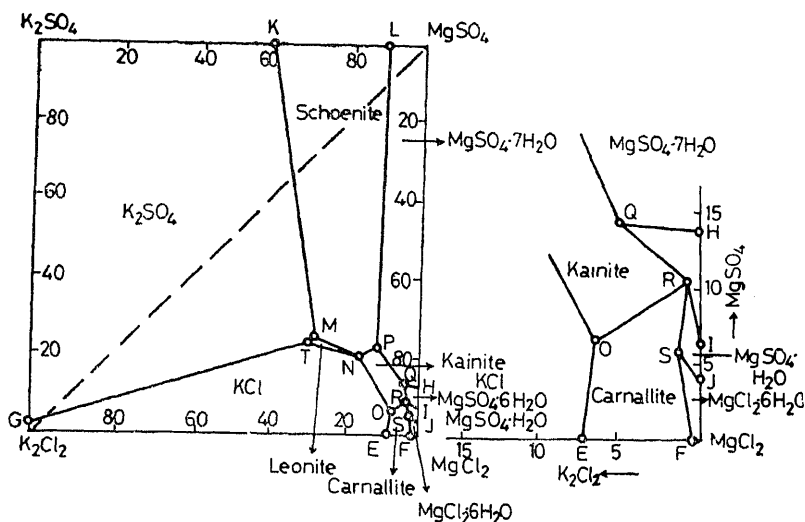


Figure 2. Study of the system $2\text{KCl} + \text{MgSO}_4 \rightleftharpoons \text{K}_2\text{SO}_4 + \text{MgCl}_2$ at 35°C (Jänecke's projection).

with a little addition of magnesium chloride hexahydrate, a situation arose where the solution was in equilibrium with three salts, the analysis of the solid phase showed the presence of leonite along with KCl and K_2SO_4 . This was represented by point T in the diagram. The continued addition of MgCl_2 to the system

KCl and kainite. Either decrease or increase of temperature for disturbing the equilibrium brought slight changes in the equilibrium but when brought back to the original conditions (*i.e.*, at 35°C), it showed the presence of four salts in the solid phase. The experiments were repeated to confirm the above equilibrium. The phenomena of supersaturation and metastable equilibrium can be ruled out by the above studies. This has been confirmed by the kainite formation which takes place at higher temperatures. Further addition of MgCl_2 produced another invariant point where carnallite was in equilibrium with kainite and KCl. On the small addition of magnesium chloride hexahydrate the formation of kieserite takes place as a fine light yellow powder. Thus again the existence of four salts takes place, *viz.*, carnallite, kieserite, kainite and $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$. The same procedure, as discussed earlier was observed. This is represented by point R on the diagram. Finally, continued addition of the $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ brought the system to the crystallization point S where the solution was in equilibrium with solid salts carnallite, keiserite and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.

The experiments were carried out by starting with point K where the solid salts were K_2SO_4 and schoenite. By adding $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ to the system, a new condition was reached when the composition of the solution was represented by point M on the diagram, which was in equilibrium with salts schoenite, leonite and K_2SO_4 . Successive addition of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ to the system shifts the equilibrium to the point N where four salts ($\text{KCl} + \text{Leonite} + \text{Schoenite} + \text{Kainite}$) are in equilibrium. This establishes the earlier experiment.

Addition of both $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ was necessary to bring about variations in the equilibrium and to reach the point P where the solid phase shows the existence of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, schoenite and kainite. The continued addition of both further produced another invariant point Q in the system. The solid phase consisted of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ and kainite. The enhanced increase of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ concentration in the system dehydrated $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ to kieserite giving rise to the point R where kieserite, kainite, $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ and carnallite were in equilibrium. This confirms the earlier result.

The points N and R where four salts in equilibrium were bound by starting with the point L and I in the diagram respectively. The other points P, Q, and O were confirmed by starting with the invariant points of the respective systems, *i.e.*, L, H, J and E.

4. Conclusions

This study establishes the various equilibria existing in the system at 35°C . It is hoped that the various discrepancies observed in the earlier data have now been eliminated and the data when applied to the recovery of potassium salts could help in understanding the above complicated system, *i.e.*, recovery of potassium as schoenite, leonite and kainite etc. The transition of schoenite to leonite at 32.5°C and at higher temperatures has been established conclusively.

Acknowledgements

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Sorption properties of oxides IX: Effect of anions on the sorption of uranium (VI) on hydrous oxides

H S MAHAL*, B VENKATARAMANI and
K S VENKATESWARLU**

Chemistry Division, Bhabha Atomic Research Centre, Bombay 400 085, India

** Reactor Chemistry Section, Chemistry Division, Chemical Group,
BARC, Bombay 400 085, India

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Abstract. Effect of anions such as nitrate, chloride, sulphate and carbonate on the sorption of U(VI), from aqueous solutions on hydrous oxides of Ti(IV), Ce(IV) Zr(IV) and Th(IV) has been studied. The sorption of U(VI) is markedly reduced in the presence of anions, like carbonate, which form strong complexes with UO_2^{2+} in solution. The results are explained in terms of a competition for free UO_2^{2+} between surface hydroxyl groups and ligands (anions) present in solution. The sorption of U(VI) on these hydrous oxides was also studied from a bicarbonate-carbonate mixture. Sorption was less under conditions when tricarboxylate complex of U(VI) was formed, but increased at higher pH values (> 9), presumably due to the formation and sorption of hydroxo complexes of U(VI).

Keywords. Quadrivalent hydrous oxides; U(VI) sorption; competitive complexation ; U(VI) carbonate complex.

1. Introduction

Sorption of U(VI) from nitrate solution on hydrous oxides of quadrivalent Ti, Ce, Zr and Th (represented as TiO_2 , CeO_2 , ZrO_2 and ThO_2) was shown to depend on the nature of the hydrous oxides, that is, the acidity of the hydrous oxide (Mahal *et al* 1981). It was shown that sorption process involved uranyl ions in the case of hydrous TiO_2 and CeO_2 and electrolyte sorption predominated in the case of less acidic hydrous oxides of Zr and Th. The effect of several anions on the sorption of U(VI) on the above hydrous oxides was investigated. The anions chosen for these studies were nitrate, chloride, sulphate and carbonate since they have varying abilities to form complexes with uranyl ion in solution. The results of these studies are presented in this paper.

2. Experimental

Preparation and characterisation of the hydrous oxides are described in detail

designated $M_2O_3(NH)$ and those prepared using $NaOH$, $MeO_2(Na)$, where $Me = Ti, Ce, Zr$ or Th . Hydrous TiO_2 prepared by homogeneous precipitation is designated $TiO_2(hp)$.

Sorption experiments were carried out at room temperature (300 K) using 0.3 g of the oxide and 25 ml of the solution containing known amounts of uranyl ion as respective salts. The mixture was kept in a mechanical shaker for 24 hr to ensure complete equilibration. Uranyl ion in solution was estimated spectrophotometrically by the peroxide method at 400 nm (Sandell 1959).

Tetrasodium tricarbonato uranilate (tr carbonate complex) was prepared by mixing uranyl nitrate and sodium carbonate solution and precipitating the tr carbonate complex formed by adding excess of methanol and washing the resultant precipitate with methanol. An aqueous solution of the tr carbonate complex thus prepared gave a spectrum which was identical with that reported in literature (Scanlan 1977).

The pH of the uranyl salt solutions was in the region of 3.5; in the case of tr carbonate complex the solution pH was around 9.

Sorption of U(VI) was also studied from a mixture of $NaHCO_3$ and Na_2CO_3 keeping the concentration of $NaHCO_3 + Na_2CO_3 \sim 0.2$ N. Initial U(VI) concentration in these solutions was 0.01 M and was added as a nitrate. The initial pH of these solutions varied between 7.3 and 10.7.

3. Results and discussion

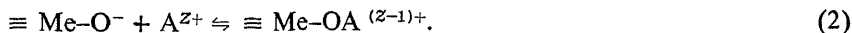
The uptake of U(VI) by hydrous oxides from a 0.01 M solution of different (uranyl) salts is given in table 1. The uptake decreased in the series: nitrate > chloride > sulphate > tr carbonate, with the exception of sulphate where in some cases slightly increased sorption was noted. The reverse of the above sequence parallels the ability of the anions to complex uranyl ion (Chernyaev 1966, p. 515).

Table 1. Sorption of U(VI) on hydrous oxides from different uranyl salt solutions (Initial $UO_2^{2+} = 0.01$ M).

Hydrous oxide	Salts used→	Uptake of uranium, mg U/g of oxide			
		Nitrate	Chloride	Sulphate	Tricarbonate
$TiO_2(hp)$		205	180	185	107
$TiO_2(NH)$		158	126	135	83
$TiO_2(Na)$		195	164	143	64
$CeO_2(NH)$		75	39	100	42
$CeO_2(Na)$		104	70	79	60
$ZrO_2(NH)$		48	30	71	31
$ZrO_2(Na)$		79	35	88	42
$ThO_2(NH)$		13	6	23	4

electrolyte sorption, as uranyl sulphate). It is generally known that the quadrivalent ions (Ti^{4+} , Ce^{4+} , Zr^{4+} and Th^{4+}) have a strong affinity for sulphate ions and forms sulphate complexes. IR spectra of the hydrous oxide equilibrated with uranyl sulphate showed absorption characteristic of sulphate ions, thus confirming the above view that sulphate ions are being sorbed.

The observed results on the effect of anions on the sorption of uranium could be explained with the help of surface complex approach proposed to describe the sorption of metal ions on hydrous oxides (Stumm *et al* 1976). If the surface hydroxyl groups of the hydrous oxide, MeO_2 , is represented as $\equiv \text{Me}-\text{OH}$, then the sorption of metal ion A^{Z+} can be written as :



It has been postulated (Stumm *et al* 1976) that $\equiv \text{Me}-\text{O}^-$ acts as a ligand and complexes sorbing metal ion, A^{Z+} , in a way similar to the complexation of A^{Z+} in solution by ligands. In situations when anions (L^-) capable of forming complexes with A^{Z+} , are present in solution, as



there is a competition for the free A^{Z+} between the surface ($\equiv \text{Me}-\text{O}^-$ groups) and the ligand (L^-) present in the solution (Theis and Richter 1980).

In the present investigation the hydrous oxides have varying acidities (Fuller, 1971) that is, the reaction represented by (1) occurs to varying degrees in each of the hydrous oxides and also the electron donor properties of $\equiv \text{Me}-\text{O}^-$ of the oxides vary, decreasing from TiO_2 to ThO_2 . In solution the anions having varying abilities to complex uranyl ion are present. For a given hydrous oxide the sorption decreases as the tendency of the anion to complex uranyl ion increases (from nitrate to carbonate), along the row in table 1. For a given anion in solution, the sorption decreases as the electron donor property of the $\equiv \text{Me}-\text{O}^-$ group or the acidity of the hydrous oxide decreases, down the column in table 1. The differences in the sorption of hydrous oxides prepared using NH_4OH and NaOH are due to the amount of hydroxyl groups present in the hydrous oxide, which depends on the alkali used for precipitation (Mahal *et al* 1981 ; Venkataramani *et al* 1978).

The above explanation is supported by the IR spectra of the hydrous oxides equilibrated with different uranyl salts. The vibration frequencies of UO_2^{2+} group observed in pure salts were 945, 943, 930 and 853 cm^{-1} , respectively, for nitrate, chloride, sulphate and tricarbonatate and the corresponding values, for hydrous TiO_2 were 900, 915, 910 and 895 cm^{-1} . A lowering of the vibration frequency of UO_2^{2+} group indicates an increase in the donor strength of the ligand (Chernyaev 1966, p. 362). In the case of hydrous TiO_2 (all the three preparations), the vibration frequency of UO_2^{2+} group decreased as a result of sorption (see above). This shows that the complexation at the surface due to $\equiv \text{Me}-\text{O}^-$ group is stronger

than with anions present in solution. In the case of tricarboxylate complex, the shift in the vibration frequency of UO_2^{2+} is not as pronounced as in other salts. This shows that the carbonate ion forms a much stronger complex with UO_2^{2+} in solution than those formed by $\equiv\text{Me}-\text{O}^-$ groups at the surface.

The absorption of UO_2^{2+} in the IR spectra were diffuse in other hydrous oxides. The shift in the vibration frequencies of UO_2^{2+} were, however, marginal for other hydrous oxides as compared to hydrous TiO_2 . It is clear that among the quadrivalent metal hydrous oxides investigated, UO_2^{2+} forms a stronger bond with the surface hydroxyl groups of hydrous TiO_2 in contrast to other oxides.

Sorption of U(VI) from solutions containing a mixture of bicarbonate and carbonate (at a total concentration of $\sim 0.2 \text{ N}$) on different hydrous oxides is given in table 2. In general, the amount of uranium sorbed is much lower than that from a solution of the salt of tricarboxylate complex (table 1). In solutions containing a mixture of bicarbonate and carbonate, the concept of competitive complexation of the free metal ion, referred to earlier (Theis and Richter 1980), between the surface $\equiv\text{Me}-\text{O}^-$ groups (equation (2)) and the carbonate ions in solution (equation (3)) is more valid than for the aqueous solution of the salt

Table 2. Sorption of U(VI) on hydrous oxides from bicarbonate-carbonate mixture (Initial $\text{UO}_2^{2+} = 0.01 \text{ M}$).

Initial $\text{CO}_3^{2-} (\text{N})$	0.0	0.01	0.05	0.06	0.08	0.11	0.15
Initial $\text{HCO}_3^- (\text{N})$	0.22	0.2	0.16	0.15	0.12	0.09	0.04
Initial pH	7.35	8.2	9.0	9.2	9.4	9.8	10.7
Hydrous oxide		Uptake of uranium, mg U/g of oxide					
$\text{TiO}_2 (\text{hp})$	25 (8.3)	22 (8.4)	14 (8.7)	14 (8.9)	14 (9.1)	14 (9.5)	25 (9.95)
$\text{TiO}_2 (\text{NH})$	13 (8.35)	11 (8.75)	11 (8.9)	13 (9.1)	13 (9.3)	13 (9.65)	25 (10.15)
$\text{TiO}_2 (\text{Na})$	9 (8.4)	2 (8.7)	2 (8.9)	2 (9.1)	2 (9.3)	2 (9.7)	22 (10.1)
$\text{CeO}_2 (\text{NH})$	1 (8.6)	1 (8.8)	1 (9.0)	1 (9.2)	2 (9.4)	2 (9.7)	22 (10.3)
$\text{CeO}_2 (\text{Na})$	*	*	*	3 (9.2)	3 (9.4)	5 (9.7)	30 (10.3)
$\text{ZrO}_2 (\text{NH})$	*	*	*	*	*	2 (9.8)	12 (10.4)
$\text{ZrO}_2 (\text{Na})$	*	*	*	*	*	*	6 (10.4)
$\text{ThO}_2 (\text{NH})$	*	*	*	*	*	*	*
$\text{ThO}_2 (\text{Na})$	*	*	*	*	*	*	*

of tricarbonic complex (table 1). In the case of bicarbonate-carbonate mixtures the ligand capable of forming a (strong and) soluble complex (that is, CO_3^{2-}) is present to a greater extent than in the aqueous solution containing the salt of the tricarbonic complex alone. The reduced sorption of uranium from as mixture of bicarbonate and carbonate (table 2) is due to the extensive complexation of U(VI) in solution by the CO_3^{2-} .

The sorption of U(VI) was higher when the initial pH was below 8.0, was minimum and nearly constant in the pH range 8.2–9.8, and increased when the pH was above 10.0 (table 2). The pH, bicarbonate and carbonate content of the equilibrated solution were determined for all hydrous oxides. The equilibrium pH values are given in table 2 and the bicarbonate and carbonate concentrations for $\text{TiO}_2(\text{hp})$, $\text{TiO}_2(\text{NH})$, $\text{TiO}_2(\text{Na})$ and $\text{CeO}_2(\text{NH})$ are presented in table 3. There was a reduction in the total alkalinity of the solution. The reduction was significant in $\text{TiO}_2(\text{hp})$ and $\text{CeO}_2(\text{NH})$. The decrease in the alkalinity indicates the release of H^+ ion, which either could be from the hydrous oxide (see equation 1) or, be a result of hydrolysis of UO_2^{2+} ion.

Based on the stability constant values of different U(VI) species, it has been estimated (Yamashita *et al* 1980), that in the pH region 8 to 10, both hydrolysed species and carbonate complexes of UO_2^{2+} coexist, the latter predominating up to a pH of 9 (Bezborodov *et al* 1976). It is also known that mixed hydroxo carbonates of UO_2^{2+} are formed at higher pH values or in weakly acidic solutions (Chernyaev 1966, chapter 2; Ciavatta *et al* 1979).

Table 3. Equilibrium concentrations of bicarbonate-carbonate mixtures for hydrous oxides of Ti and Ce.

Initial CO_3^{2-} (N)	0.0	0.01	0.05	0.06	0.08	0.11	0.15
Initial HCO_3^- (N)	0.22	0.20	0.16	0.15	0.12	0.09	0.04
Equilibrium concentration, N							
TiO ₂ (hp)							
CO_3^{2-}	0.016	0.016	0.023	0.034	0.045	0.070	0.095
HCO_3^-	0.182	0.175	0.164	0.151	0.136	0.108	0.079
TiO ₂ (NH)							
CO_3^{2-}	0.029	0.036	0.047	0.059	0.070	0.099	0.131
HCO_3^-	0.181	0.171	0.156	0.142	0.128	0.095	0.065
TiO ₂ (Na)							
CO_3^{2-}	0.018	0.032	0.043	0.059	0.07	0.099	0.131
HCO_3^-	0.196	0.181	0.165	0.147	0.133	0.100	0.062
CeO ₂ (NH)							
CO_3^{2-}	0.025	0.027	0.032	0.050	0.06	0.088	0.091

The higher sorption of U(VI) in low carbonate solutions (up to 0.01 N) (table 2) could be due to the presence to a lesser extent of tricarboxylate complex, the sorption of U(VI) probably occurring with the breaking of the carbonate complex, releasing carbonate into the solution (table 3) and thus increasing the pH of the equilibrated solution (table 2). The nearly constant and minimum sorption could be explained as due to the predominance of tricarboxylate complex in the pH range 9-10. The increased uranium sorption at carbonate concentration above 0.1N is probably due to the sorption of hydrolysed species of UO_2^{2+} (Yamashita *et al* 1980).

Different mechanisms have been proposed to explain the sorption of uranium on hydrous oxides from tricarboxylate complex. It is proposed that the tricarboxylate complex breaks down and the uranyl ion is sorbed on the hydrous oxides (Davies *et al* 1965; Yamashita *et al* 1980). Another mechanism involves the partial breaking of the tricarboxylate complex and the sorption of a dicarboxylate complex on the oxide (Jaffrezic-Renault *et al* 1980). Our results indicate that the sorption of uranium from carbonate solutions involves only a partial breaking of the tricarboxylate complex. However, the data obtained in the present study (tables 2 and 3) could not be fitted into suitable mathematical relations describing the sorption process, as has been attempted by others (Davies *et al* 1965; Jaffrezic-Renault *et al* 1980). This is because, apart from the sorption of U(VI), other reactions (such as hydrolysis) taking place in solution also have altered the carbonate-bicarbonate equilibrium.

4. Conclusion

There is a growing interest in selecting a sorbent for the recovery of uranium from sea water (Davies *et al* 1965; Jaffrezic-Renault *et al* 1980; Schwochau *et al* 1977; Yamashita *et al* 1980). Uranium is present in trace levels (about 3 ppb) in sea water as tricarboxylate complex. The present study indicates that the $\equiv\text{Me}-\text{O}^-$ groups of the hydrous oxides do not possess enough electron donor properties to compete with carbonate ion to complex uranyl ion, so that uranium could be selectively sorbed on hydrous oxides. In addition under actual sea water conditions, the alkaline earth metal ions, which are present in much larger amounts, would compete for the sorption sites on hydrous oxides and still reduce the sorption of uranium. If hydrous oxides are to be used on a large scale for the recovery of uranium from sea water, their sorption capabilities should be modified and improved by orders of magnitude by suitable preparative techniques.

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Electrochemical reduction of copper(II) galacturonate

ROBERT PAYNE and ROBERT J MAGEE

Department of Inorganic and Analytical Chemistry, La Trobe University,
Bundoora, Melbourne, Victoria 308, Australia

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Abstract. The complexes formed in the interaction between copper(II) and α - and β -galacturonic acid, in the pH range 2.5–11.0, have been investigated by means of d.c. polarography and cyclic voltammetry. With α -galacturonic acid, no complex is formed with copper up to pH 6. Between pH 6 and about 9.5, a complex is formed in solution. Above pH 9.5, the complex appears to break up releasing the ligand. In the case of β -galacturonic acid, no complex is formed until pH 3.5, and persists in solution up to a pH of about 9.5. A second complex forms above pH 6.9 and co-exists with the first complex up to pH 9.5. The complexes formed with both forms of galacturonic acid were studied and the stability constant of the copper α -galacturonate determined.

Keywords. Electrochemical studies; polarography; cyclic voltammetry; stability constant; copper(II) α - and β -galacturonate.

Introduction

As a result of investigations on the method of uptake of copper by certain species of bacteria (Payne *et al* 1981) in which the metallic species was found to be bound to uronic acids, it was necessary to investigate the interaction of copper(II) with galacturonic acid over a wide pH range. In a recent report (Payne and Magee 1982), the authors have presented results for the reaction of copper(II) with glucuronic acid. In the present paper, a similar study for copper(II) and galacturonic acid is reported.

Experimental

Polarographic and cyclic voltammetric studies were carried out on the AMEL 71-Multipolarograph System and the Princeton Applied Research (PAR) 170 Electrochemistry System. Results were plotted on a Hewlett-Packard 7040 A X-Y Recorder. pH was recorded on an ET1572 Digital pH meter. The polarographic cell had a three electrode configuration consisting of a saturated calomel reference electrode and a platinum counter electrode. For the d.c. polarographic measurements, a glass capillary dropping electrode (DME) was used; for the cyclic voltammetric studies, the hanging mercury drop electrode (HMDE) was used.

141 Polarimeter. Galacturonic acid exists in the α - and β -form, with the following properties :

α -galacturonic acid	Mpt 159° C	Optical rotation + 107 $\rightarrow$ 51.9° (H ₂ O)
β -galacturonic acid	Mpt 164-166° C	Optical rotation + 31.1 $\rightarrow$ 56.7°

Galacturonic acid (Sigma) which was mainly in the α -form was purified to give the pure α -form of the acid using the method of Isbell and Frush (1943). Similarly, the β -form was obtained in a pure state. The purity of both forms were checked by optical rotation measurements and by means of the melting points. From the β -form, sodium galacturonate was prepared by direct titration of the β -galacturonic acid with sodium hydroxide. However, α -galacturonic acid was used as the acid without conversion to the sodium salt, as it has been shown (Isbell and Frush 1943) that sodium galacturonate consists of the β -D-galacturonic acid.

Copper nitrate was used as the source of Cu(II) ions. Stock solutions of copper nitrate were standardised with EDTA using a potentiometric end-point determination.

All results were obtained at an ionic strength of 0.74 M NaClO₄. pH values were checked before and after recording the voltammograms.

3. Results and discussions

3.1. Studies on α -galacturonic acid

3.1a *Polarographic investigations—the effect of pH on $E_{1/2}$ values* : To 30 ml of 0.276 M α -galacturonic acid and 1 ml of a 2×10^{-2} M solution of copper nitrate in a polarographic cell was added 9.0 ml of 2.822 M NaClO₄ solution. The pH was varied over the range 2.5-11.0. In each case polarograms were recorded in the potential range +0.2 to -0.7 volt.

Up to pH 6, a single wave (wave I) was obtained, which was clearly indicative of the reduction of free Cu(II) ions in a 2-electron reduction step (figure 1a). At pH 6, a second wave (wave II) began to appear following wave I, with $E_{1/2} \cong -0.145$ V (figure 1b). As the pH was increased, wave I decreased in size, while wave II continued to increase. By pH 8.0, the free Cu(II) wave had disappeared, but wave II persisted up to a pH of about 9.5 (figure 1c). Over the pH range, the $E_{1/2}$ of wave II varied from -0.145 to -0.197 volt. Above pH 9.5, wave II began to disappear rapidly due to the growth of a wave which was suspected to be a ligand wave (figure 1d). Investigations carried out on the ligand alone and in the presence of Cu(II) at pH 10.00 confirmed the presence of a large ligand wave.

3.2. Wave II

3.2a. *Variation of limiting current with height of Hg column* : The effect of height of the Hg column on the limiting current of wave II was examined. Limiting currents were found to be proportional to $\sqrt{h}$, indicating diffusion control.

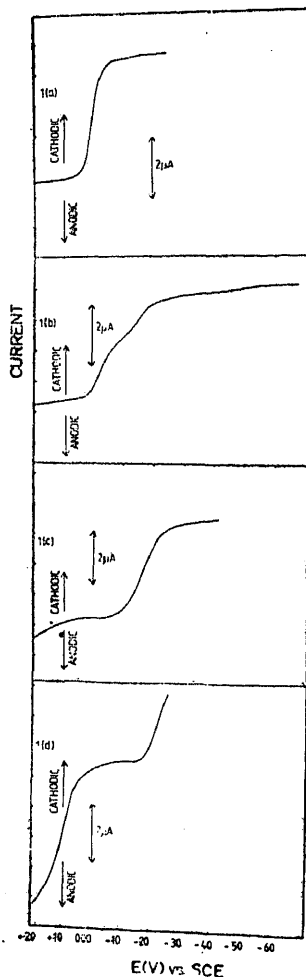


Figure 1. D.C. polarograms at DME at varying pH values of Cu^{II} -galacturonate (a) complexation, 0.635 M NaClO_4 . $T = 25.0^\circ \text{C}$, $h = 62.0 \text{ cm}$; 0.008% Triton X-100 added. (a) $\text{pH} = 4.51$; (b) $\text{pH} = 6.46$; (c) $\text{pH} = 8.92$; (d) $\text{pH} = 9.92$.

3.2b. *Log plot analysis*: Using the same conditions as above ($\text{pH } 8.9$), a log plot analysis was applied to wave II. The plot of E vs $\log (i/i_a - i)$ gave a straight line with a slope of -31 mV , which gives a value of $n = 2$ for the number of electrons involved in the reduction.

3.2c. $E_{1/2}$ vs $\log C(X)$: With the pH at 8.2 , the effect of change in concentration of ligand on $E_{1/2}$ was examined. A linear plot was obtained over the concentration range 0.0 to 0.276 M in α -galacturonic acid. The copper concentration was held at $5 \times 10^{-4} \text{ M}$. The linear plot indicates the presence of a single complex formed at this pH , i.e. for wave II. From the relationship

complex formed with α -galacturonic acid is more stable than that formed with β -glucuronic acid.

The value of p was calculated to be approximately 2 (1.95).

3.2d. $E_{1/2}$ vs pH : In the region at which wave II forms, the pH was varied from pH 6.0 to 11.0. At each pH , the $E_{1/2}$ value was determined and a plot of $E_{1/2}$ vs pH obtained. The plot was curved but consisted of two distinct linear portions. The first over the pH range of 6.0 to approximately 9.0; the second at pH values greater than pH 9.0. The two straight lines were analysed using the relationship

$$E_{1/2} = E^\circ - \frac{0.0591}{n} m pH + \frac{0.0591}{n} \log \left(\frac{f_o C_o}{f_r C_r} \right).$$

From the slopes of the two plots, each of which is equal to $(-0.0591/n)m$, where m = number of hydrogen ions involved, m was calculated. For the pH region 6-9, i.e., the region in which the complex represented by wave II forms, m was found to be equal to 2. For the region $pH > 9$, i.e., the region in which the complex breaks up releasing the ligand, m was found to be equal to 1.

4. Cyclic voltammetry

Cyclic voltammograms were obtained under the same conditions as for the d.c. polarography, pH being varied over the range of 4-10. Figure 2 shows the results obtained. Below $pH \cong 6.0$, the voltammogram consisted of one cathodic peak (peak I_{pc}) and one anodic peak (peak I_{pa}) (figure 2a). The voltammogram showed clearly that only free Cu(II) ions were present in solution ($E_{pc} = -0.03$ V). Above pH 6 a second cathodic peak began to appear at a more negative potential than the Cu peak (peak II_{pc}). On the anodic sweep at this pH the main oxidation peak of copper was still present and no other major peak except the semblance of a peak with E_{pa} around +0.045 V (peak III) (figure 2b). As the pH was increased further, the second peak on the cathodic sweep increased in size with a corresponding reduction of the copper peak, until by about pH 8 it was fully developed ($E_{pc} = -0.205$ V) and the copper peak had disappeared. On the anodic sweep one major peak was present: this did not occur at the same potential as the original copper oxidation peak but, although close was at a more negative potential ($E_{pa} \cong -0.025$ V). The same small peak ($E_{pa} \cong +0.065$ V) as mentioned above still persisted but was more clearly marked (figure 2c). Above pH 9, there were clear indications of the break up of the complex (figure 2d) with a rapid decrease in the major cathodic and anodic peaks obtained at the lower pH values and the rapid increase of a peak with E_{pc} around +0.09 V. This was found to correspond to the free ligand. At first sight, it looked as if the reduction represented by peak II (i.e. wave II in d.c. polarography) was irreversible as there appeared to be no current on the anodic sweep. However, on further investigations during

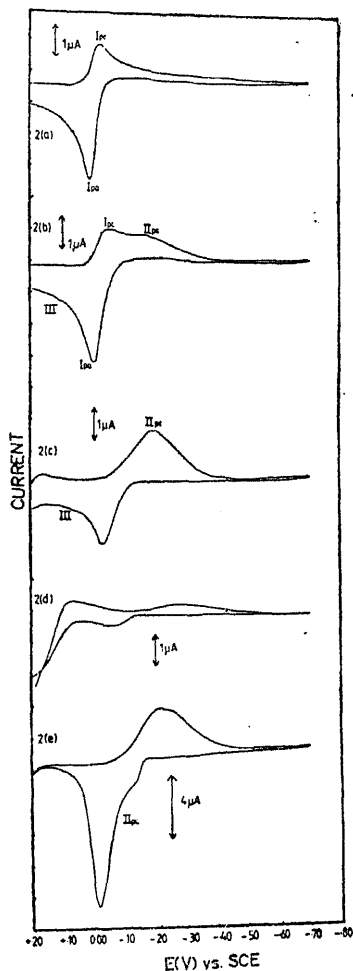


Figure 2. Cyclic voltammograms at HMDE (scan rate -0.020 v/s, $T = 25^\circ\text{C}$), 0.635 M NaClO_4 in the presence of nitrogen at varying pH values. (a) $\text{pH} = 4.27$; (b) $\text{pH} = 6.81$; (c) $\text{pH} = 8.0$; (d) $\text{pH} = 9.57$; (e) $\text{pH} = 8.0$.

which the scan rate was varied, it was found that at very slow scan rates, the major anodic peak at $E_{pa} \approx +0.025$ V had a shoulder ($E_{pa} = -0.138$ V) which appeared at faster scan rates (figure 2e). It would appear that this anodic peak is the oxidation peak of the main reduction peak (peak II) ΔE_p averaged over a number of experiments was found to be 83 mV indicating a quasi-reversible reaction in agreement with d.c. polarography. The main anodic peak ($E_{pa} \approx +0.25$ V) was examined more closely. It was found that this peak of sharp symmetry increased in magnitude with increasing scan rate and decreasing concentration while anodic potentials became more negative with increasing scan rate. This peak therefore showed the characteristics of an adsorption wave.

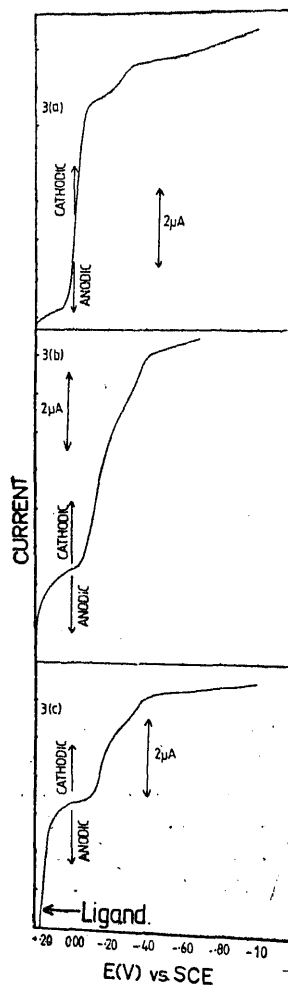
complex of the ligand or the ligand itself. On examination of the free ligand a peak was obtained at the same potential.

5. Studies on β -galacturonic acid

5.1. Polarographic investigations—the effect of pH on $E_{1/2}$ values

To 30 ml of 0.1309 M sodium galacturonate and 1 ml of a 2×10^{-2} M solution of copper nitrate in a polarographic cell was added 9.0 ml of 0.635 M NaClO_4 solution. The pH was varied over the range 2.5–11.0. In each case, polarograms were recorded in the potential range +0.2 to –0.700 volt.

In the pH range 2.5–3.5, a single wave (wave I) was obtained with $E_{1/2}$ around –0.03 volt. This wave was clearly indicative of free Cu(II) in a 2-electron reduction step. Above pH 3.5, a second wave (wave II) (figure 3a) appeared



Following wave I and persisted up to pH values around 9. Above pH 6, wave I began to decrease, while a third wave (wave III) began to appear at pH values greater than 6.9 between wave I and wave II (figure 3b). Waves II and III persisted together up to pH values greater than about 9. Both disappeared together at pH values greater than 9.5, being replaced by a single wave which was found to be due to the reduction of the ligand (figure 3c). Wave I never completely disappeared until, like waves I and III, it was replaced by the ligand wave. The polarography of the copper β -galacturonate was never as clear as that of the copper α -galacturonate: the waves tended to run into each other, making measurements difficult. $E_{1/2}$ values for the three waves varied as follows over the pH range studied—wave I -0.026 to -0.04 volt; wave II -0.292 to -0.311 volt; wave III -0.123 to -0.140 volt. It is presumed that waves II and III present the formation of copper complexes of the β -galacturonic acid.

1a. *Wave II*: The effect of height of the Hg column on the limiting current was examined and indicated diffusion control under the polarographic conditions. From a log-plot analysis, the number of electrons involved in the reaction was found to be 2, while the slope indicated a reversible reduction. Because of proximity of the waves it was not possible to determine unequivocally the effect of concentration of ligand on $E_{1/2}$.

Cyclic voltammetry

Cyclic voltammograms were obtained at varying pH values under the same conditions as used for the d.c. polarographic studies.

Below pH 3.5, the voltammogram showed only one peak, clearly indicating the presence of free Cu(II) ions (figure 4a). Above about pH 3.5 a second peak (peak II₀) appears existing alongside peak I due to the Cu(II) (figure 4b). Both peaks exist up to a pH greater than 5, when a third peak (peak III) begins to develop, initially as a shoulder on peak I (figure 4c).^{*} By pH 7.5–8.0 the free Cu(II) disappears leaving peaks II and III. Above pH around 9, peaks II and III decrease and are ultimately replaced by a ligand peak. At all stages of development, peak III was small and broad, making measurements impossible. For peak II, the effect of voltage scan rate was examined at a pH 6.9. Results are shown in table 1.

It will be seen that, in agreement with the polarographic data, the reduction is quite reversible at low scan rates.

On the anodic sweep of all the voltammograms, one large anodic wave is present. It is presumed that initially this represents the anodic oxidation of Cu(II) and an adsorption peak. At high pH values, when the copper cathodic peak has disappeared this anodic peak is still present and is an adsorption peak. However, unlike the situation with α -galacturonic acid, it was never possible to separate an adsorption peak and the electroactive peak.

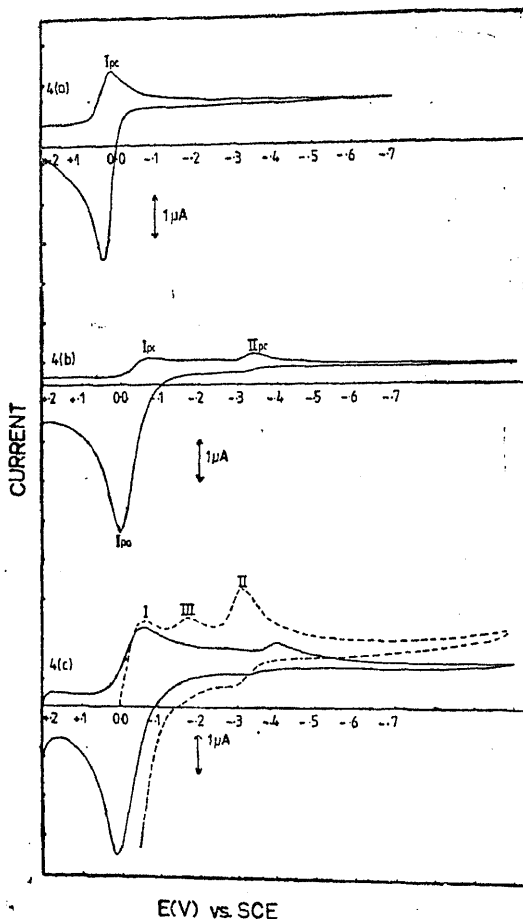


Figure 4. Cyclic voltammograms at HMDE (scan rate -20 mV/sec, $T = 25^\circ \text{C}$ in aq. solution, 0.635 M NaClO_4 in presence of nitrogen at varying pH values. (a) pH = 3.0 ; (b) pH = 4.90 ; (c) pH = 6.87.

Table 1. Effect of voltage scan rate on peak II.

Scan rate V sec^{-1}	E_{p_0} vs SCE $\pm 0.005 \text{ V}$	E_{p_0}	ΔE_p (mV)	I_{p_0} (mA) $\pm 0.05 \text{ mA}$	I_{p_0}	I_{p_0}/I_{p_0}
0.005	-0.329	-0.299	0.030	0.146	0.124	0.86
0.010	-0.330	-0.298	0.032	0.276	0.228	0.83
0.020	-0.331	-0.281	0.050	0.268	0.197	0.74
0.050	-0.350	-0.287	0.063	0.413	0.285	0.69

Comparison of the results obtained with copper and α -galacturonic acid and copper and β -glucuronic acid (Payne *et al* 1981) shows, especially in the cyclic voltammetric results, a remarkable similarity except for the fact that in the latter case, a third, irreversible peak is obtained above pH 7.4. However, in the case of copper and α -galacturonic acid, voltammograms at pH's > 7.6 do show a weak indication of a peak at $E_p > 0.3$ volt. This peak, however, never did achieve the magnitude of that for copper and β -glucuronic acid.

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Metal complexes of isonicotinic acid hydrazide

H SANKE GOWDA* and R JANARDHAN

Department of Post-graduate Studies and Research in Chemistry, University of Mysore, Manasagangotri, Mysore 570 006, India

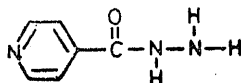
MS received 22 September 1981; revised 29 June 1982

Abstract. Complexes of platinum(IV), ruthenium(III), rhodium(III), iridium(III), gold(III), dioxouranium(II), zinc(II), cadmium(II), mercury(II) and manganese(II) with isonicotinic acid hydrazide were prepared and characterized on the basis of analytical, conductometric, magnetic susceptibility and spectral data. Platinum(IV), ruthenium(III), rhodium(III), iridium(III), dioxouranium(II) and manganese(II) form six-coordinate complexes while gold(III), zinc(II), cadmium(II) and mercury(II) form four coordinate complexes.

Keywords. Metal complexes; isonicotinic acid hydrazide; characterization.

1. Introduction

Metal complexes of isonicotinic acid hydrazide (INH) are of great importance because of their antituberculous properties. The limited information available on the structural aspects of metal-INH complexes prompted the authors to study and report on the complexes of Pt(IV), Ru(III), Rh(III), Ir(III), Au(III), $\text{UO}_2(\text{II})$, Mn(II), Zn(II), Cd(II) and Hg(II) with INH, which has the following structure.



2. Experimental

2.1. Materials

Chlorides of platinum(IV), ruthenium(III), rhodium(III), iridium(III) and gold(III) were obtained from Arora Mathew Limited, Calcutta. Chlorides of zinc(II), cadmium(II), mercury(II) and manganese(II) and uranyl nitrate and INH (Analar BDH) were used as such. Acetone and ethanol were purified by standard methods.

or the chloride of M^1 [$M^1 = \text{Zn(II)}, \text{Cd(II)}, \text{Hg(II)}$ or Mn(II)] was treated with 50 ml of 0.02 M solution of INH in the respective solvent. The complexes of Pt(IV), Ru(III), Rh(III), Ir(III) and Au(III) are precipitated immediately while the complexes of $\text{UO}_2(\text{II})$, Zn(II), Cd(II), Hg(II) and Mn(II) get precipitated after heating on a boiling water bath for one hour. The solid complexes were filtered, washed several times with the respective solvent and dried over anhydrous calcium chloride in a desiccator.

2.3. Analytical and physical measurements

Elemental analysis of the complexes was carried out by conventional methods. The Gouy method was used to measure the magnetic susceptibilities at room temperature 27°C. Visible spectra and conductance measurements were recorded on 10^{-4}M solutions of the complexes in dimethylformamide (DMF). Infrared spectra were recorded on KBr discs containing INH and its complexes.

2.4. Results and discussion

All the complexes are stable up to 250°C. Platinum(IV), rhodium(III), iridium(III), dioxouranium(II) and manganese(II) complexes are yellow, gold(III) complex is black, ruthenium(III) complex is brown and zinc(II), cadmium(II) and mercury(II) complexes are white in colour. The complexes are practically insoluble in water. Platinum(IV), rhodium(III), iridium(III), dioxouranium(II) and manganese(II) complexes are slightly soluble in DMF and dimethyl sulfoxide (DMSO), ruthenium(III) and gold(III) complexes are soluble and zinc(II), cadmium(II) and mercury(II) complexes are insoluble in common organic solvents.

Analytical data for the complexes show that the composition of the complexes is $[(\text{INH})_2\text{PtCl}] \text{Cl}_2$; $[(\text{INH})_2\text{MCl}_2] \text{Cl}$ [where $\text{M} = \text{Ru(III)}, \text{Rh(III)}$ or Ir(III)]; $[(\text{INH})_2\text{UO}_2](\text{NO}_3)_2$; $[(\text{INH})_2\text{MnCl}_2]$; $[(\text{INH})\text{AuCl}_2] \text{Cl}$; and $[(\text{INH})\text{MCl}_2]$ [where $\text{M} = \text{Zn(II)}, \text{Cd(II)}$ or Hg(II)].

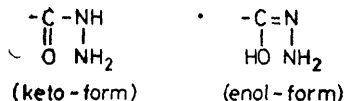
The molar conductance values of platinum(IV), ruthenium(III), rhodium(III), iridium(III), dioxouranium(II) and gold(III) complexes indicate that they are electrolytes in DMF. The electrolytic behaviour of the other complexes could not be studied due to their insolubility in DMF.

The diamagnetism of platinum(IV), rhodium(III), iridium(III) and dioxouranium(II) complexes reflect the favourable octahedral geometry of these complexes. The diamagnetic behaviours of zinc(II), cadmium(II) and mercury(II) complexes point out their preferred tetrahedral geometry. The diamagnetism of gold(III) complex suggests a square planar geometry. The magnetic moment value of 2.2 B.M. observed for the ruthenium(III) complex, though rather high for one unpaired electron, is nevertheless in the right range for octahedral ruthenium(III) complexes for which a considerable orbital contribution is expected (Ruiz-Ramirez and Stephenson 1975). Further, the presence of non-equivalent stoichiometric sites in the complex molecule suggests a slight distortion in the regular octahedral geometry of this complex. Manganese complex forms a high spin complex having

a magnetic moment value of about 5.94 B.M. which suggests an octahedral arrangement of the ligand molecules around the central metal ion.

The visible spectra of platinum(IV), ruthenium(III), rhodium(III), iridium(III), dioxouranium(II) and manganese(II) complexes show charge transfer bands at 380, 385, 360, 375, 365 and 400 nm, respectively. The $d-d$ bands were not observed probably due to their masking by the intense charge-transfer bands. The visible spectra of zinc(II), cadmium(II) and mercury(II) complexes could not be recorded due to their insolubility. Gold(III) complex showed three bands at 600, 520 and 445 nm and these bands have been assigned to $^1A_{1g} \rightarrow ^3A_{2g}$, $^1A_{1g} \rightarrow ^3E_g$ and $^1A_{1g} \rightarrow ^1A_{2g}$ transitions respectively which are characteristic of square planar gold(III) complexes (Gajendragad and Agarwala 1975).

A shift in the bands at 3430 and 1715 cm^{-1} due to $\nu(\text{NH}_2)$ and $\nu(\text{C=O})$ respectively in the infrared spectrum of INH by about 90 cm^{-1} in the spectra of its complexes indicates the involvement of the nitrogen atom of the NH_2 group and the oxygen atom of the C=O group in coordination (Sahni *et al* 1977). Further, a shift in the $\nu(\text{C-N})$ band observed at 1490 cm^{-1} in the INH spectrum by about 50 cm^{-1} in the spectra of its complexes indicates the preference of the keto form to the enol form of the ligand for coordination.



Coordination through the oxygen atom of the C=O group resulted in a decrease in its double bond character and new bands observed around $1,100\text{ cm}^{-1}$ in the spectra of the complexes are assigned to the C=O stretching vibrations. Low frequency bands in the $420\text{--}500\text{ cm}^{-1}$ and $520\text{--}610\text{ cm}^{-1}$ regions in the spectra of the complexes are assigned to the $M\text{---}N$ and $M\text{---}O$ modes respectively (Olliff and Odell 1967, 1967; Olliff and Odell 1968).

A strong band at 920 cm^{-1} and a weak band at 870 cm^{-1} in the UO_2 (II) complex are assigned to the ν_3 asymmetric and ν_1 symmetric stretching frequencies which are characteristic of the uranyl ion (Selbin and Angew 1966). Further, the appearance of ν_1 symmetric stretching frequency indicates that the uranyl ion is almost linear (Sacconi *et al* 1958).

Acknowledgement

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Synthesis of some zero-valent complexes of iron via aryldiazzenato cationic complexes

S VANCHEESAN

Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

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Abstract. Bis (triphenylphosphine) dicarbonylaryldiazzenato-iron, $[\text{Fe}^0 (\text{ArN}_2) (\text{CO})_2 (\text{PPh}_3)_2]^+ (\text{I})$, reacts in a solution of LiOEt under nitrogen atmosphere, with a variety of group V donor ligands, substituting the aryldiazzenato ligand, ArN_2^+ . The effect of substitution on the stretching frequency of CO is discussed.

Keywords. Aryldiazzenato cationic complex; substitution reactions; zero-valent complexes; iron.

Introduction

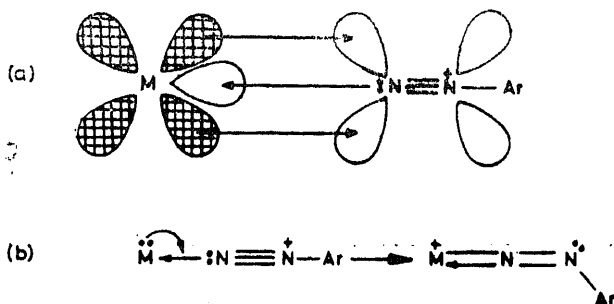
Substituted derivatives of iron pentacarbonyl such as $\text{L}_2\text{Fe}(\text{CO})_3$ ($\text{L} = \text{Phosphine}$) react with nitrosyl chloride (Crooks and Johnson 1968) or nitrosonium hexaphosphosphate (Johnson and Segal 1972) to give salts of a nitrosyl cation of type, $[\text{NO Fe}(\text{CO})_2 (\text{PPh}_3)_2]^+ \text{X}^-$ ($\text{X} = \text{Cl}^-$ or PF_6^-). Since the nitrosonium and zonium cations are isoelectronic, arylazo complexes of iron might be accessible to the reactions of $\text{L}_2\text{Fe}(\text{CO})_3$ with diazonium tetrafluoroborates. The first arylazo complex of iron, $(\text{R} \cdot \text{C}_6\text{H}_4\text{N}_2) \text{Fe}(\text{CO})_2 \text{L}_2]^+ \text{BF}_4^- (\text{I})$ was reported by Sher and Sutton (1973). Aryldiazzenato ligand has a strong resemblance to nitrogen. Besides, applications in biological fixation and activation of dinitrogen (Sher and Sutton 1973; Einstein and Sutton 1972, 1973), aryldiazzenato complexes offer a novel route for the synthesis of mixed ligand complexes of zero-valent iron.

Stirring a solution of I in lithium ethoxide (prepared by reacting stoichiometric quantities of lithium and ethanol) with a variety of ligands L , resulted in the new complexes listed in table 1.

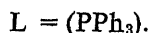
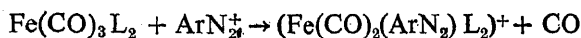
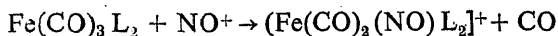
Discussion

Aryldiazzenato ligand is analogous to nitrosyl ligand. This can be viewed as a free electron donor or as the cation ArN_2^+ coordinated through the σ -lone pair

change as oxygen goes up to sp^2 occurs. But the more populated $2p\pi$ orbital of ArN_2^+ leaves the angle at N^2 (nitrogen away from the metal M in figure 1) close to 180° (a) whereas the valence bond prediction is 120° (b).



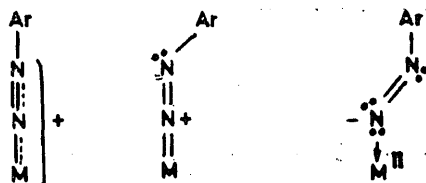
The substitution of CO in $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ by ArN_2^+ merits special consideration (Johnson and Segal 1972; Carrol and Lalor 1973).



In view of the positive charge it is doubtful whether they could act as Lewis bases towards the electron-rich metal centre. However it is sensible to consider an electrophilic attack at the electron-rich low-valent metal atom and the displacement of CO which occurs as a result of the competition between the electrophilic ArN_2^+ or NO^+ and the incumbent ligand CO for the metal d -electrons.

When a metal complex reacts with an aryldiazonium salt, the product is formed by the displacement of another ligand. Such replacement by ArN_2^+ maintains the 18 electron configuration. ArN_2^+ being an electrophile, attack at an electron rich CO is favoured. Thus $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ undergoes replacement of one CO group by ArN_2^+ to form $(\text{Fe}(\text{ArN}_2)(\text{CO})_2(\text{PPh}_3)_2)^+$, the formal oxidation state of iron being zero (Fisher and Sutton 1973).

For a coordinated diazenato ligand two limiting structures are possible (figure 2; Mingos and Ibers 1971). Structures (a) and (c) are analogous to NO^+ and NO^- . (c) is related to (b) by a formal transfer of two electrons from metal to ligand so that the ligand behaves as ArN_2^- . Structure (c) has no geometric equivalent in nitrosyl chemistry.



The complex I has TBP geometry (Lalor and Pauson 1970) similar to that of $(\text{CO})_3(\text{PPh}_3)_2$. Very high values of νN_2 (1720 cm^{-1}) suggest a low degree of back-bonding to the ArN_2^+ ligand. The diazonium cation could be considered formally to be either 3e donor towards Fe^{I} or 2e donor to Fe^0 . Consistency in ν_{CO} values for various X-substituted aryl group favours the latter view. Infra-red spectra of the complexes (1) through (6) exhibit two peaks in the carbonyl region expected for *cis* dicarbonyl groups (table 1 ; figure 3). For the phosphite complex which is more π -acidic than phosphine, one can expect an increase in the CO bond order and νCO value which is in agreement with observed values of νCO . On the contrary complex (6) with a *p*-tolyl group, electron donating CH_3 adds to the electron population of $\text{CO}\pi^*$ orbital and naturally ν_{CO} is shifted to lower region. Ditertiary phosphine and arsine substitute two phosphine groups from I which is expected for a bidentate ligand.

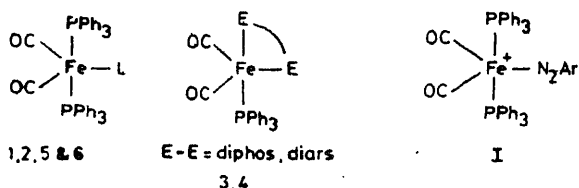


Table 1. Analytical and important infra-red spectral data of complexes.

Complex	Found (calcd) %		CO (cm^{-1})*
	C	H	
$(\text{CO})_2(\text{PPh}_3)_2(\text{AsPPh}_3)$	70.9 (71.35)	4.72 (4.78)	1978 (S), 1916 (V·S)
$(\text{CO})_2(\text{PPh}_3)_2(\text{SbPh}_3)$	68.05 (67.97)	4.57 (4.55)	1975 (S), 1955 (V·S)
$(\text{CO})_2(\text{PPh}_3)_2(\text{diphos})$	71.56 (71.52)	5.02 (5.05)	1980 (S), 1920 (V·S)
$(\text{CO})_2(\text{PPh}_3)_2(\text{Diars})$	64.5 (64.2)	4.52 (4.54)	1982 (S), 1922 (V·S)
$(\text{CO})_2(\text{PPh}_3)_2\{(\text{PhO})_3\text{P}\}$	70.8 (71.0)	4.72 (4.75)	1995 (S), 1934 (V·S)
$(\text{CO})_2(\text{PPh}_3)_2\{(p\text{-tolyl})\text{Ph}_2\text{P}\}$	75.2 (75.01)	5.12 (5.15)	1968 (S), 1903 (V·S)

Reactions of $\text{Fe}(\text{CO})_2(\text{PPh}_3)_3$ in solution has already been studied (Vancheesan 1982). It is established that this complex dissociates to a coordinately unsaturated, 16e complex, $\text{Fe}(\text{CO})_2(\text{PPh}_3)_2$, which readily reacts with L to form $\text{Fe}(\text{CO})_2(\text{PPh}_3)_2 L$. It is the axial phosphine which is replaced by L . Such substitution reaction is possible in the case of arsine and stibine complexes also, provided L is sterically favoured. When compared to $\text{Fe}(\text{CO})_2(\text{PPh}_3)_3$, complexes 1, 2 and 6 are expected to exchange L more readily, because the axial ligands arsine, stibine and diphenyl *p*-tolyl phosphine are sterically less favourable than phosphine to be accommodated in the axial position. It is difficult to predict the behaviour of diphos and diars complexes, 3 and 4. Further studies on the reactions of the complexes are in progress.

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Spectrophotometric study of the formation of adducts between $U(TTA)_4$ and some neutral organo sulphoxide donors

A RAMANUJAM, N M GUDI, M N NADKARNI,
S K PATIL*† and V V RAMAKRISHNA†

Fuel Reprocessing Division, Bhabha Atomic Research Centre, Bombay 400 085,
India

† Radiochemistry Division, Bhabha Atomic Research Centre, Bombay 400 085,
India

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Abstract. Adduct formation between $U(TTA)_4$ and neutral organosulphoxide donors dibenzyl sulphoxide (DBSO), dimethyl sulphoxide (DMSO), dihexyl sulphoxide (DHSO) and dioctylsulphoxide (DOSO) was studied by spectrophotometry. Each of these donors form a 1 : 1 adduct with $U(TTA)_4$. The adduct formation constants ($\log \beta_{AB}$) were calculated from spectral changes and were found to be 3.10 (DBSO), 3.23 (DMSO), 3.62 (DHSO) and 3.64 (DOSO).

Keywords. Solvent extraction ; synergism ; $U(TTA)_4$; neutral donor adducts.

Introduction

The synergism in the extraction of metal ions from aqueous media by organic solvents containing a mixture of a betadiketone (HA) and a neutral donor (S) is mainly due to the formation of adducts in the organic medium between the metal betadiketonate and the neutral donor. This is especially true when the aqueous and the organic media used are such that the neutral donor alone is not capable of extracting the metal ion to a significant extent. Among tetravalent actinides, formation of such adducts have been reported for thorium, uranium, plutonium and plutonium. The adduct formation constants are usually estimated from the solvent extraction data. Such data, however, can be obtained directly from spectral changes accompanying the adduct formation and we have earlier reported such results on U(IV) (Patil *et al* 1979a; Patil and Ramakrishna 1979b; Ramakrishna *et al* 1980), Np(IV) (Sajun *et al* 1981) and Pu(IV) (Ramakrishna *et al* 1979; Patil *et al* 1980). In continuation of these studies, the adduct formation between $U(TTA)_4$ (TTA—thenoyltrifluoroacetone ligand) and the neutral organosulphoxide donors DBSO, DMSO, DHSO and DOSO, in benzene, has been investigated and the results are reported here.

The compound U(TTA)_4 was prepared as described (Ramakrishna *et al* 1980). The sulfoxides were prepared and purified (Mohanty and Reddy 1975). HTTA was obtained from M/s. E. Merck, Germany and used after drying over P_2O_5 . Analar benzene was used as such.

2.2. Procedure

The experimental procedure used was the same as described (Patil *et al* 1979a). Benzene solutions of U(TTA)_4 , in the presence of ten-fold excess of HTTA, and suitable concentration of the desired neutral donor (S) were prepared so as to get solutions having varying ratios of $(\text{S})/(\text{U(IV)})$ but the same concentration of U(IV) . Absorption spectra of these solutions were recorded using a Cary 14 spectrophotometer.

3. Results and discussion

The absorption spectrum of U(TTA)_4 and the changes caused to it by the addition of different amounts of DMSO are shown in figure 1. Similar changes were observed with other sulfoxides as well. The presence of well-defined isosbestic points in the spectra shown in figure 1 suggests that there are only two absorbing species in the system, obviously, U(TTA)_4 and its adduct $\text{U(TTA)}_4\cdot\text{S}$, in analogy with the adducts reported using the organo phosphorus donors. Following the same procedure as reported earlier, the adduct formation reaction can be written as



for which the equilibrium constant is given by

$$\beta_{\text{AB}} = \frac{[\text{U(TTA)}_4\cdot\text{S}]}{[\text{U(TTA)}_4][\text{S}]} = \frac{(E_1 - E)}{(E - E_2)[\text{S}]} \quad (2)$$

where

$$[\text{S}] = [\text{S}]_{\text{total}} - \frac{(E_1 - E) \times C}{(E_1 - E_2)} \quad (3)$$

where C = the total concentration of U(IV) , E_1 = molar extinction coefficient of U(TTA)_4 alone, E_2 = molar extinction coefficient of $\text{U(TTA)}_4\cdot\text{S}$ alone and E = molar extinction coefficient of the mixture.

The absorption spectrum of U(TTA)_4 obtained in the absence of any added S was used to get the value of E_1 at the desired wavelength. The value of E_2 was derived from the spectrum when $(\text{S})/(\text{U(IV)})$ is high so that any further increase in this ratio did not cause any observable change in the spectrum, thereby suggesting the almost complete conversion of U(TTA)_4 to its adduct. Typical data giving the absorbance values and the values of β_{AB} calculated from them, with the donor DMSO are given in table 1. A summary of the adduct formation constant values obtained in this work are given in table 2 alongwith the literature data.

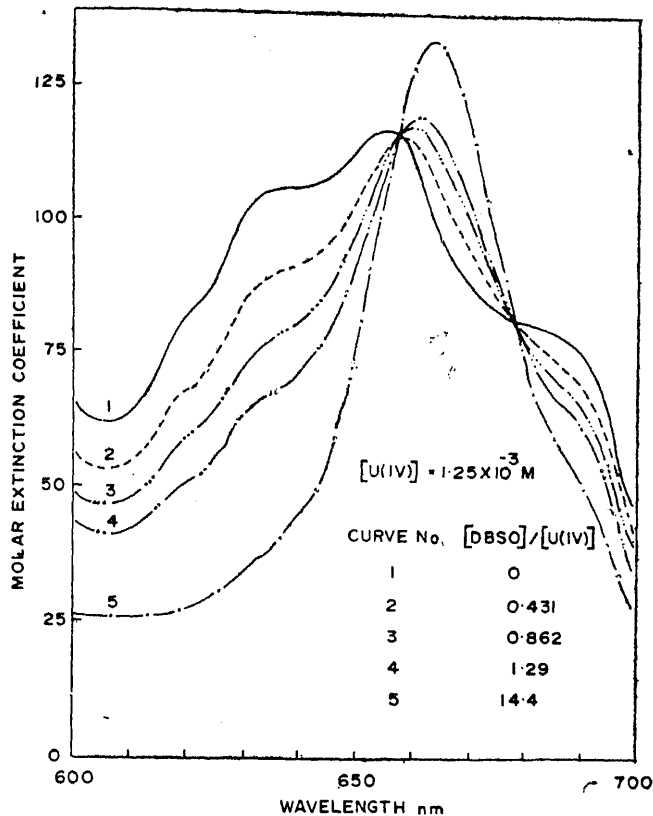


Figure 1. Absorption spectra of $U(TTA)_4$ with varying (DBSO).

Table 1. Spectrophotometric data on the adduct formation between $U(TTA)_4$ and DBSO in benzene.

$[U(IV)] = 1.25 \times 10^{-3} M$

		Molar extinction coefficient (E) at nm			$\log \beta_{AB}$ at, nm		
		570	580	590	570	580	590
0	(E_1)	176	125	88	...	...	...
4	(E_2)	103	58	29	...	...	...
431		158	108	73	3.18	3.16	3.15
862		146	98	64	3.08	3.08	3.09
29		135	88	54	3.14	3.13	3.16
72		130	83	51	3.09	3.08	3.08
15		127	80	48	3.06	3.04	3.04

Table 2. Summary of the β_{AB} values for the formation of 1:1 adducts between $U(TTA)_4$ and neutral donors in benzene.

Neutral donor	$\log \beta_{AB}$
Tri- <i>n</i> -octyl phosphine oxide (TOPO)	6.23
Tri phenyl phosphine oxide (TPPO)	4.72
Di- <i>n</i> -butyl butyl phosphonate (DBBP)	4.04
Dicotyl sulphoxide (DOSO)	3.64
Dihexyl sulphoxide (DHSO)	3.62
Dimethyl sulphoxide (DMSO)	3.23
Dibenzyl sulphoxide (DBSO)	3.10
Tri- <i>n</i> -butyl phosphate (TBP)	3.04
Tri-iso octyl thio phosphate (TIOTP)	1.04
Methyl-iso butyl ketone (MIBK)	0.1

The β_{AB} values of the sulphoxide adducts of $U(TTA)_4$ are seen to follow the increasing order that $DBSO < DMSO < DHSO < DOSO$ which is in conformity with their expected basicity values (Nikitin *et al* 1976). The structures of these adducts are expected to be identical to those discussed earlier, with uranium atom having a coordination number of nine in them (Patil *et al* 1979c).

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Chelation ion-exchange properties of salicylic acid-urea-formaldehyde copolymers

R M JOSHI and M M PATEL*

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar 388 120, India

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Abstract. Chelation ion-exchange properties of copolymers prepared from salicylic acid, urea and formaldehyde by condensation in presence of acid catalyst were studied for Cu^{2+} , Fe^{3+} , UO_2^{2+} , Mn^{2+} , Zn^{2+} and Co^{2+} ions. A batch equilibration method was adopted to study the selectivity of metal ion uptake. This method involved the measurement of distribution of a given metal between the copolymer sample and a solution containing the metal ions. The study was carried out over a wide pH range and in media of various ionic strengths. The copolymer showed a higher selectivity for UO_2^{2+} , Cu^{2+} and Fe^{3+} ions than Mn^{2+} , Co^{2+} and Zn^{2+} ions.

Keywords. Chelation ion exchange ; batch equilibration ; distribution ratio.

Introduction

Salicylic acid and its bi-substituted derivatives are well-known complexing agents and find many applications in analytical chemistry of inorganic species. The salicylic acid formaldehyde polymer has been reported to show a chelation ion-exchange capacity (Donaruma 1962 ; Degeiso *et al* 1962a, 1963). It is obvious that copolymers prepared from salicylic acid are also a subject of an extensive investigation for their chelation properties.

We report in this paper the systematic study of the selectivity and capacity of salicylic acid(S)-urea(U)-formaldehyde (F) copolymers (SUF) in the ion-exchange reaction. The SUF copolymers used here were prepared by condensation of (S) and (U) in different molar-proportions with (F) in presence of aq. HCl at 100°C for 5 hr (Joshi and Patel 1981). The batch equilibration method (Gregor *et al* 1952, 1953) was employed to study the effect of various electrolytes on the metal uptake, rate of metal uptake and the distribution ratio of the metal ions between polymeric material and solution at different pH.

of S : U : F to be equal to (1 : 1 : 2) and (3 : 1 : 4) respectively ; by condensation in the presence of 2M aq. HCl at 100° C for 5 hr (Joshi and Patel 1981). The copolymers were washed with large amounts of hot water, soxhlet extracted with ether and purified by dissolving in 8% NaOH and reprecipitating with 1 : 1 (V/V) conc. HCl/water. Finally the copolymers were washed with hot water and dried in vacuum at room temperature. The purified copolymers were finely ground to pass a 300 mesh screen and used in all experiments described in the present text.

2.2. *Determination of metal uptake in the presence of different electrolytes*

In order to study the effect of the nature of the electrolyte and its concentration on the amount of the metal ions taken up by the copolymer sample, SUF-1 copolymer sample 25 mg each, were weighed into a 100 ml glass stoppered conical flask. 44 ml of each 0.01, 0.05, 0.1, 0.5 and 1 M NaNO_3 were added to the samples. The pH of the suspensions was adjusted to 2.5 by addition of 0.1 M HNO_3 or 0.1 M NaOH and stirred for a period of 24 hr at room temperature. This treatment would swell the copolymer samples. Then 0.1 M metal solution (1 ml) was added to each one of the above suspensions and the pH was adjusted to the required value by the use of appropriate concentration (1 M-0.01 M) of NaOH or HNO_3 . The slurries were stirred at room temperature continuously for 24 hr, filtered and washed with distilled water. The filtrates and washings were combined and the metal was estimated by titrating against standard EDTA. A blank experiment was similarly carried out without adding the copolymer sample. The blank was also estimated for the metal ion content. The metal ion uptake by the copolymer in the presence of sodium nitrate of known concentrations was obtained from difference between the blank reading and the reading in the actual experiment. This experiment was repeated in the presence of different electrolytes of known concentrations for different metal ions (table 1). The same procedure was applied to the SUF-2 copolymer sample.

2.3. *Evaluation of the rate of metal uptake*

With a view to estimate the time required to reach the state of equilibrium under given experimental conditions with each metal ion, a series of experiments of the type described above were carried out. The metal ion Fe^{3+} , Cu^{2+} and UO_2^{2+} taken up by the chelating copolymer was estimated from time to time (table 2) at 25° C in the presence of 44 ml of 1M NaNO_3 solution, while the selectivity of Mn^{2+} , Co^{2+} , and Zn^{2+} was determined in the presence of 44 ml of 0.01 M NaNO_3 solution, as the copolymer in the presence of these last three metal ions was found to be more stable with respect to solubility than in the 1 M NaNO_3 . It is assumed that under the given conditions, the state of equilibrium is established in 24 hr. The rate of metal uptake is expressed as percentage attainment of the state of equilibrium by expressing it as the amount of metal ion taken up after a certain time in relation to that in the state of equilibrium (cf. table 2).

2.4. Evaluation of distribution of metal ions at different pH

The distribution of each one of the six metal ions Cu^{2+} , UO_2^{2+} , Fe^{3+} , Mn^{2+} , Zn^{2+} and Co^{2+} between polymer phase and aqueous phase was estimated at 25°C . 1M NaNO_3 was used for the first three metal ions and 0.01M NaNO_3 was used for the last three metal ions. The experiments were carried out as described above in the pH range 1 to 7. The distribution coefficient D was calculated according to

$$D = \frac{\text{amount of metal on the copolymer}}{\text{amount of metal in the solution}} \times \frac{\text{volume of solution}}{\text{weight of copolymer}}$$

The results are shown in table 3.

3. Results and discussion

3.1. Effect of electrolytes on the metal uptake

It is known that chelation reactions can be carried out most efficiently in the presence of a buffer system of higher capacity to maintain a certain pH value. At the same time metal-buffer reactions can shift the position of the equilibrium of metal polymer interaction especially where chelates of low stability are formed. Hence, to find out which electrolyte system has maximum metal uptake, the influence of ClO_4^- , NO_3^- , Cl^- and SO_4^{2-} was examined at various concentrations on position of the equilibrium. Table 1 reveals that the amount of Cu^{2+} , UO_2^{2+} and Fe^{3+} taken up by SUF-1 and SUF-2 copolymer samples increases with increasing concentration of ClO_4^- , NO_3^- and Cl^- and decreases with increasing concentration of SO_4^{2-} (Degeiso *et al* 1962a), whereas, uptake of Mn^{2+} , Co^{2+} and Zn^{2+} ions by the above copolymers increases with decreasing concentration of ClO_4^- , NO_3^- , Cl^- and SO_4^{2-} . This may be explained in terms of stability constants (Degeiso *et al* 1962a) of the chelates with these copolymers. Sulphate might form rather strong chelates with Fe^{3+} , UO_2^{2+} and Cu^{2+} ions, while perchlorate, nitrate and chloride might form weak chelates and therefore might not influence the position of the Fe^{3+} , UO_2^{2+} and Cu^{2+} salicylate equilibrium as much as sulphate. This trend has also been observed by others (Degeiso *et al* 1962a; Patel and Pate, 1979). The amount of metal uptake is more in SUF-2 than in SUF-1. However, the difference in uptake in both the copolymers is less as compared to their difference in molar ratio of salicylic acid : urea. Our results indicate that for the copolymers under study, higher pH was not suitable when concentrated electrolytes were used. The effect was more predominant in SUF-2 than in SUF-1 copolymer. The copolymer containing a higher salicylic acid-to-urea molar ratio was less stable with respect to solubility in concentrated electrolyte solution at higher pH. Hence it may be concluded that a higher concentration of urea in the copolymer improves, to some extent, the stability of the copolymer when used as an ion-exchanger, without affecting the metal uptake significantly.

3.2. Rate of metal uptake

Table 1. Evaluation of the effect of different electrolytes in the uptake of several metal ions $[M^{n+}(\text{NO}_3)_n] = 0.1 \text{ mol. l}^{-1}$

Metal ion	Electrolyte mol. l ⁻¹	pH	Weight in meq × 10 of the metal ion taken up in the presence of			
			NaClO ₄	NaNO ₃	NaCl	Na ₂ SO ₄
Cu ²⁺	1.00		0.28 ^b (0.45) ^a	0.23 ^b (0.29) ^a	0.26 ^b (0.31) ^a	0.065 ^b (0.14) ^a
	0.50		0.2 (0.34)	0.14 (0.21)	0.16 (0.26)	0.077 (0.18)
	0.10	5.0	0.17 (0.24)	0.1 (0.18)	0.11 (0.24)	0.14 (0.24)
	0.05		0.16 (0.19)	0.075 (0.17)	0.095 (0.21)	0.16 (0.26)
	0.01		0.15 (0.19)	0.07 (0.16)	0.08 (0.2)	0.19 (0.265)
Fe ³⁺	1.00		0.30 (0.36)	0.15 (0.22)	0.18 (0.24)	0.04 (0.11)
	0.50		0.28 (0.34)	0.13 (0.19)	0.14 (0.20)	0.06 (0.11)
	0.10	2.0	0.25 (0.32)	0.12 (0.17)	0.12 (0.18)	0.1 (0.13)
	0.05		0.24 (0.31)	0.11 (0.15)	0.11 (0.17)	0.12 (0.17)
	0.01		0.21 (0.30)	0.09 (0.14)	0.10 (0.15)	0.13 (0.20)
UO ₂ ²⁺	1.00		0.39 (0.48)	0.35 (0.44)	0.37 (0.46)	0.22 (0.28)
	0.50		0.35 (0.44)	0.32 (0.40)	0.34 (0.42)	0.27 (0.33)
	0.10	4.0	0.27 (0.36)	0.25 (0.32)	0.32 (0.31)	0.32 (0.38)
	0.05		0.24 (0.33)	0.23 (0.28)	0.29 (0.26)	0.35 (0.41)
	0.01		0.22 (0.32)	0.23 (0.26)	0.26 (0.25)	0.35 (0.43)

Na ⁺	0.50	0.015 (0.035)	0.02 (0.03)	0.015 (0.025)	0.025 (0.03)
	0.10	0.03 (0.08)	0.025 (0.06)	0.035 (0.045)	0.03 (0.045)
	0.05	0.08 (0.11)	0.07 (0.08)	0.06 (0.075)	0.05 (0.065)
	0.01	0.09 (0.13)	0.075 (0.09)	0.08 (0.095)	0.075 (0.085)
	1.00	0.02 (..)	0.01 (..)	0.015 (..)	0.01 (..)
Ca ²⁺	0.50	0.03 (0.035)	0.025 (0.035)	0.045 (0.02)	0.025 (0.025)
	0.10	0.055 (0.075)	0.045 (0.06)	0.04 (0.05)	0.045 (0.055)
	0.05	0.06 (0.09)	0.06 (0.075)	0.06 (0.065)	0.055 (0.065)
	0.01	0.085 (0.11)	0.07 (0.08)	0.075 (0.09)	0.06 (0.08)
	1.00	0.03 (0.035)	0.025 (0.025)	0.01 (0.02)	0.01 (0.025)
Zn ²⁺	0.50	0.045 (0.05)	0.04 (0.045)	0.02 (0.035)	0.025 (0.03)
	0.10	0.06 (0.065)	0.05 (0.06)	0.03 (0.045)	0.03 (0.035)
	0.05	0.07 (0.08)	0.055 (0.06)	0.05 (0.065)	0.05 (0.06)
	0.01	0.08 (0.09)	0.065 (0.07)	0.07 (0.085)	0.06 (0.075)

polyte solution : 44 ml, volume of metal ion solution : 0.1 mol, I^{-1} ; volume : 1 ml ; time : 24 hr ; temp : room temp.

Table 2. Comparison of the rates of metal (M^{n+}) ion uptake^a.

Time in hr	Percentage of the amount of metal ions taken up ^b					
	Cu^{2+}	Fe^{3+}	UO_2^{2+}	Mn^{2+}	Co^{2+}	Zn^{2+}
0.5	62 ^c (71) ^d	51 ^c (55) ^d	40 ^c (46) ^d	19 ^c (21) ^d	13 ^c (15) ^d	16 ^c (16) ^d
1	71 (80)	64 (74)	69 (71)	33 (41)	23 (28)	28 (35)
2	85 (85)	83 (84)	93 (86)	41 (60)	42 (45)	45 (58)
3	91 (89)	93 (92)	98 (94)	59 (69)	55 (60)	57 (69)
4	94 (92)	96 (94)	99 (96)	70 (81)	64 (70)	68 (78)
5	94 (95)	98 (95)	99 (98)	78 (90)	73 (83)	80 (87)
6	95 (96)	98 (96)	99 (98)	81 (94)	81 (91)	87 (94)
7	95 (96)	98 (97)	...	93 (94)	89 (93)	91 (94)
8	...	...	...	85-	94-	95-

^a $[M^{n+}(NO_3)_n] = 0.1$ mol./l.⁻¹; volume : 1 ml. $[NaNO_3] = 1$ mol./l.⁻¹; volume: 44 ml for Cu^{2+} , Fe^{3+} and UO_2^{2+} ions. $[NaNO_3] = 0.01$ mol./l.⁻¹; volume : 44 ml for Mn^{2+} , Co^{2+} and Zn^{2+} ions; pH: 5 for Cu^{2+} ; 2.0 for Fe^{3+} , 4.0 for UO_2^{2+} and 5.5 for Mn^{2+} , Co^{2+} and Zn^{2+} ; temp; room temp.

^b Related to the amount of metal ions in the state of equilibrium (100%).

^c SUF-1; ^d SUF-2.

the metal ions in the aqueous solution in contact with the polymer, keeping in view the stability of the copolymers under study it was not possible to study the rate of metal uptake at high pH and in same concentration of electrolytes as discussed above of the various metal ions under study. The rate of uptake of Cu^{2+} during the first hour in both the copolymers is the highest. After 1 hr the rates of uptake of UO_2^{2+} and Fe^{3+} increase and are found to be higher than that of Cu^{2+} ion. Equilibrium is reached in the shortest possible time of 4 hr. For Cu^{2+} the equilibrium time is 5 hr. Mn^{2+} , Zn^{2+} and Co^{2+} require almost the same time 7 hr. The overall rate of metal uptake follows the order $UO_2^{2+} > Fe^{3+} > Cu^{2+} > (Mn^{2+} \approx Co^{2+} \approx Zn^{2+})$ for both the copolymers, but it is comparatively higher in SUF-2 than in SUF-1 copolymer (table 2).

3.3. Distribution ratio of metal ions at different pH

The effect of pH on the amount of metal ion distributed between two phases can be explained by the examination of results shown in table 3. The results indicate that the relative amount of metal ions taken up by the polymeric material increases with increasing pH of the medium. The study was carried out only up to pH 7 to prevent hydrolysis of the metal ions at higher pH. Both the copolymers are taking up UO_2^{2+} more selectively than any other metal ions under study. Cu^{2+} and Fe^{3+} ions are also taken up by the copolymers more selectively than Mn^{2+} , Co^{2+} and Zn^{2+} which are taken up poorly. Hence, the results of this type of study are helpful in selecting the optimum pH for a selective uptake of a parti-

Table 3. Distribution ratios D^a of different metal ions as a function of the pH.

pH	Distribution ratio of the metal ions					
	Cu ²⁺	Fe ³⁺	UO ₂ ²⁺	Mn ²⁺	Co ²⁺	Zn ²⁺
1.5	..	141.5 ^b (218.9) ^c	...	...	...	...
1.75	...	232.9 (320.2)	...	...	...	...
2.0	...	360.0 (528.6)	30.5 (46.1)	...	...	...
2.5	55.6 (92.7)	519.4 (651.0)	...	...	...	...
3.0	...	...	128.5 (163.6)	36.7 (65.0)	27.4 (74.0)	18.0 (46.0)
3.5	117.5 (334)	...	473.6 (489.1)	...	...	...
4.0	385.0 (616.1)	...	786.8 (1118.9)	65.2 (104.0)	74.9 (140.0)	46.0 (74.9)
5.0	553.0 (699.0)	...	...	149.0 (222.0)	114.8 (156.0)	94.0 (135.0)
5.5	...	...	...	...	156.0 (233.0)	...
6.0	...	...	...	188.9 (268.0)	...	135.0 (188.9)
7.0	...	...	...	222.4 (305)	...	...

$^a D = \frac{\text{amount of metal on the copolymer}}{\text{amount of metal in the solution}} \times \frac{\text{volume of solution}}{\text{weight of copolymer}}$; $[M^{n+} (NO_3)_n] = 0.1$

mol./l⁻¹; volume : 1 ml; NaNO₃ = 1 mol l⁻¹; volume : 44 ml for Cu²⁺, Fe³⁺ and UO₂²⁺; NaNO₃ = 0.01 mol. l⁻¹; volume 44 ml for Mn²⁺, Co²⁺ and Zn²⁺; temp.: room temp.; time : 24 hr (equilibrium state).

^b SUF-1;

^c SUF-2.

UO₂²⁺, at which the distribution ratio D of Fe³⁺ is 528 and that of UO₂²⁺ is 46.

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The study of *cis*- and *trans*-2 butene using mass spectrometry

EZZAT T M SELIM

Nuclear Physics Department, Atomic Energy Establishment, Cairo, Egypt

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Abstract. Using mass spectrometric technique, the effect of geometrical isomerism on the first and higher appearance energy values for $C_4H_8^+$, $C_4H_7^+$ and $C_3H_3^+$ ions obtained from *cis*-2-butene and *trans*-2-butene is reported. The structure in the ionization efficiency curves (studied for 9 eV above threshold) for the same ions obtained from the two isomers is reported and compared. It is believed that at threshold $C_4H_7^+$ fragment is formed from the two isomers as methallyl ion. For $C_3H_3^+$ fragment formed from the *cis*-isomer at threshold the proposed structure is the propargyl ion with ΔH_f equal to 279.4 kcal/mole while for that ion obtained from *trans*-isomer the proposed structure is the allenyl ion with ΔH_f equal to 296.6 kcal/mole.

Keywords. *Cis*-2-butene ; *trans*-2-butene ; mass spectrometry ; geometrical isomerism.

1. Introduction

The study of the effect of electrons on the ionization and fragmentation of geometrical isomers had been carried out by Natalis (1965). He concluded that the ionization energies of *cis*- and *trans*-isomers being the same imply that the same amount of energy is provided to the two types of molecules by the impinging particle, electron or photon. Also, geometrical isomerism disappears by fragmentation of ionized molecules, the extra energy content of *cis*-isomers due to steric conformation is released and used in the fragmentation process.

Cis- and *trans*-2-butene isomers had been investigated by Meisels *et al* (1970) using electron impact and by Morrison using the second derivative technique. They reported the appearance energies at threshold only of $C_2H_6^+$ and $C_2H_4^+$ fragments obtained from the two geometrical isomers.

Recently, Sunner (1980) using charge transfer technique reported the appearance energies at threshold only for 16 fragments obtained from *cis*-2-butene. His results also show that it is possible to distinguish isomers by charge transfer mass spectrometry, even if the molecular ions isomerize prior to fragmentation, by exploiting differences in the ionization probabilities.

The purpose of the present article is to report the effect of geometrical isomerism

9 eV above threshold. The structures in the ionization efficiency (IE) curves for the same ions obtained from the two isomers are reported and compared.

2. Experimental technique

The IE data are obtained using the Atlas CH-4 mass spectrometer with a normal electron impact ion source (AN-4). The condition of measurements, experimental technique and calibration of energy scale had been reported previously (Selim *et al* 1978 ; Selin 1976). The experimental results are taken in the form of IE curves, i.e. ionization yield against accelerating voltage for the electrons (varied by 0.1 eV steps). These directly measured IE curves are then smoothed by seven-points smoothing method (Savitzky and Golay 1964). The smoothed data are treated by the energy distribution difference (EDD) technique (Winter *et al* 1966) by means of which the effective electron energy distribution can be reduced thus allowing an accurate determination of appearance energies and fine structure in the curves. The value of the constant b characterizing the EDD technique is taken to be 0.63 eV. This value of b is chosen so as to give the best results for Ar ionization energy value.

A computer technique is developed and used for determining the exact position of the breaks in the ion intensity difference curves. The technique is based upon straight line fitting procedure (Selim *et al* 1978 ; Allenson and Sedgwick 1968). In many cases, however, a step function may occur in the curves and can be detected when the sequence of increasing slopes is broken. The step function regions are further examined by manual plotting of the data. The numerical values of Student t used in the present study are that corresponding for 95% confidence limit which is proved to be suitable for the present results.

3. Results and discussion

The ionization efficiency (IE) curves for the ions, studied for 9 eV above threshold are given in figures 1-6. The initial portion of each curve is plotted on a magnified scale above the initial one. The ionization and appearance energies obtained from IE curves of the studied ions together with similar results previously reported by different authors using different techniques are reported in table 1. The values given are the average of six determinations while the errors quoted are the standard deviations. Only reproducible ionization and appearance energies are reported in the table. In table 2 the differences between the ionization energies as well as differences between appearance energies for the same ions obtained from the two isomers are reported. Heats of formation corresponding to the first and second appearance energies for the ions studied are also reported in table 2.

3.1. $C_4H_8^+$ ($m/z = 56$) parent ion

The measured first ionization energies for *cis*- and *trans*-2-butene are 9.26 and 9.25 eV respectively. The ionization energy for the two isomers is established (Watanabe *et al* 1962 ; Dewar and Worley 1969) at 9.13 eV. It is generally

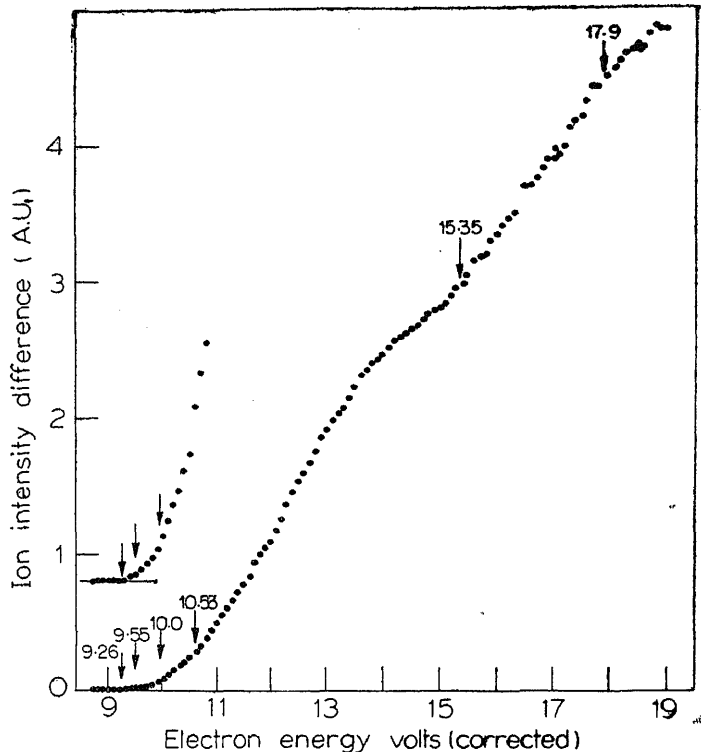


Figure 1. The ionization efficiency curve for *cis*-2-butene parent ion ($m/z = 56$).

Higher energy levels have been detected in the IE curves of *cis*- and *trans*-butene and reported in table 1. The differences between the values of the corresponding energy levels for the two isomers are within the limits of experimental errors (table 2). The only available similar energy levels in the literature compare with are those reported by Dewar and Worley (1969) at 11.28, 12.4 (13.74), (14.75), 16.07 and (18.84) eV for *cis*-2-butene and at 11.46, 12.58 and 13.99 eV for *trans*-2-butene. No possible correlation can be obtained between the energy levels reported by these authors and that obtained from the present IE curves for the two isomers. However, many authors (White *et al* 1974, Kimura *et al* 1975) had detected vertical second ionization energy for *cis*-butene at 2.3 eV and for *trans*-2-butene at 2.5-2.6 eV above the corresponding vertical first ionization energy.

3.2. $C_4H_7^+$ ($m/z = 55$) fragment ion

The IE curve for $C_4H_7^+$ fragment obtained from *cis*-2-butene shows a somewhat sharp rise at the threshold while the curve for the same fragment from the *trans*-isomer exhibits a short tail at the threshold. The values measured for the appearance energy for $C_4H_7^+$ ion from *cis*- and *trans*-2-butene isomers are 11.51 and 11.50 eV, respectively. The value 11.51 eV is in good agreement with ph

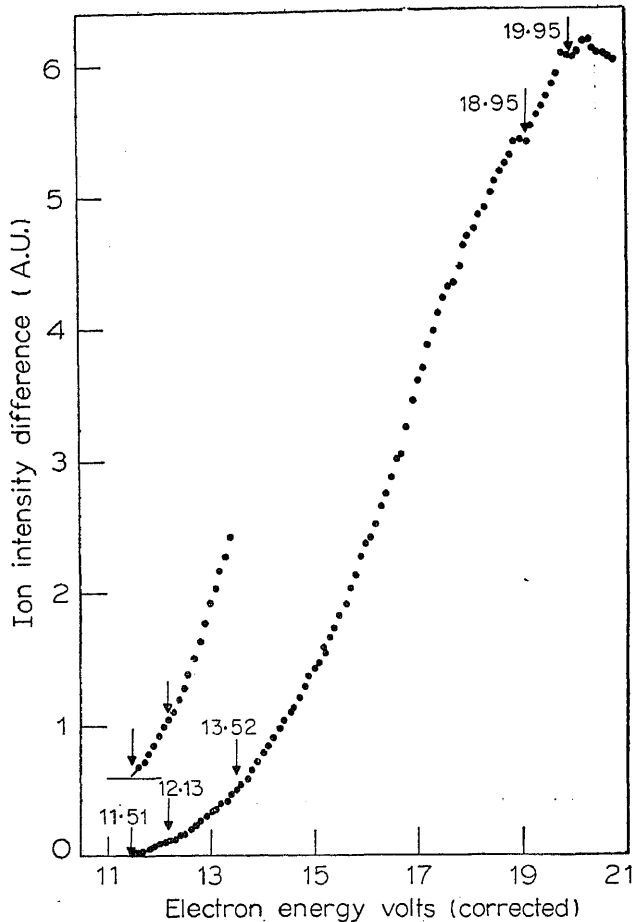


Figure 2. The ionization efficiency curve for fragment ion ($m/z = 55$) from *cis*-2-butene.

$C_4H_7^+$ fragment from *trans*-2-butene the only available value in the literature is the value reported early by Dibelar (1947) (11.24 eV).

The structure in IE curves for *cis*- and *trans*-2-butene are similar except for the higher appearance energy 12.50 eV which appears only in *trans*- isomer curve and appearance energy 13.52 eV which appears only in the *cis*-isomer curve.

The fragment $C_4H_7^+$ is formed from the two isomers by simple removal of H atom from $C_4H_8^+$ molecular ion. This process requires no reverse activation energy and the kinetic shift associated with the detectable threshold is believed to be small as a result of using : (a) zero draw-out potential and (b) high sensitivity electron multiplier as detector in the present study. The calculated ΔH_f values for $C_4H_7^+$ fragment obtained at threshold from *cis*- and *trans*-2-isomer respectively are 211.7 and 210.9 kcal/mole which may indicate that the same ion structure is

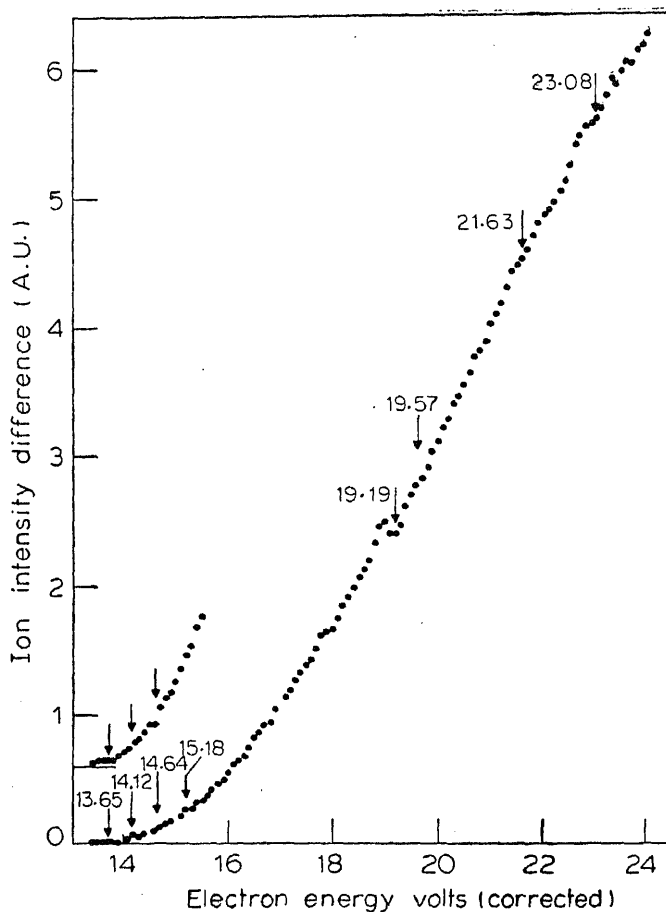


Figure 3. The ionization efficiency curve for fragment ion ($m/z = 39$) from *cis*-2-butene.

Lossing (1972) from the ionization energy of methallyl radical. The present I_0 value for the ion suggests a kinetic energy shift of about 7 kcal/mole in the appearance energy of the ion. However, Lossing (1972) reported the value 226 kcal/mole for methallyl ion obtained from different sources with kinetic shift only 2 kcal/mole.

It is possible that at higher energy than the threshold $C_4H_7^+$ fragment is formed a cyclic $C_3H_4CH_3^+$ ion with ΔH_f value (Franklin *et al* 1969) around 221 kcal/mole. There is evidence supporting this from the IE curves of $C_4H_7^+$ fragments obtained from both *cis*- and *trans*-isomers. These curves reveal second appearance energy* at 12.13 and 12.22 eV respectively and the corresponding calculated I_0 values are 226 and 227 kcal/mole. Taking into account a presumed small

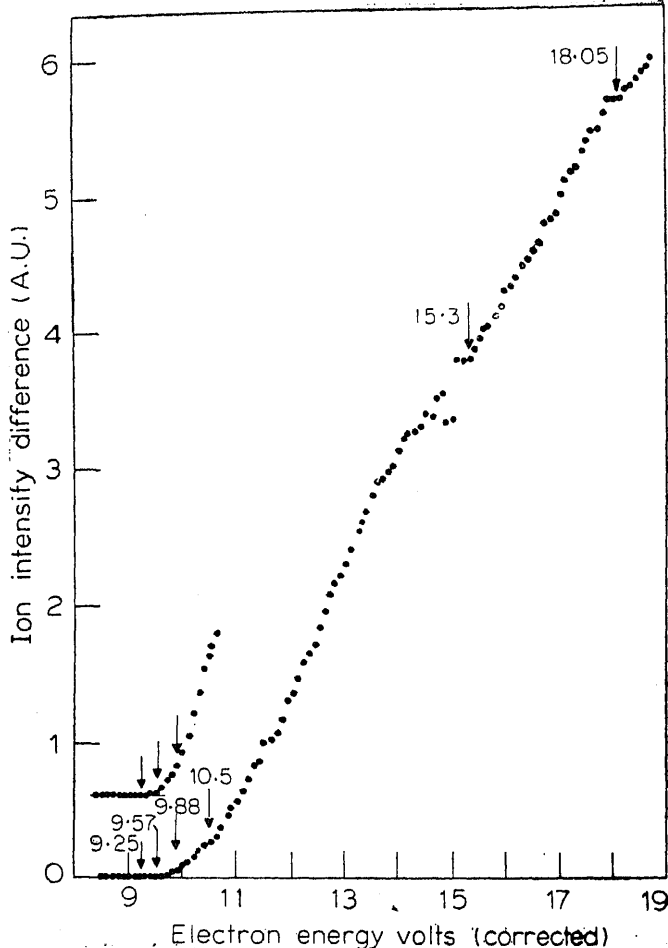


Figure 4. The ionization efficiency curve for *trans*-2-butene parent ion ($m/z =$

suggest that ΔH , values 226 and 227 kcal/mole correspond well to cyclic C_3H_4C structure with ΔH , value equal to 221 kcal/mole as reported by Franklin *et al.* (1969).

3.3. $C_3H_3^+$ ($m/z = 39$) fragment ion

The IE curves for the fragment ion obtained from the two isomers exhibit long tails at the threshold. The first appearance energy for $C_3H_3^+$ fragment obtained from the *cis*-isomer is measured at 13.65 eV and is in good agreement with previously reported values (13.75, Omura 1961 and 13.80, Dibejar 1947) while the ion obtained from the *trans*-isomer is measured at 14.44 eV and in reasonable agreement with the only previously reported value 14.20 eV (Dibejar 1947). The difference between the appearance energy values for $C_3H_3^+$ frag-

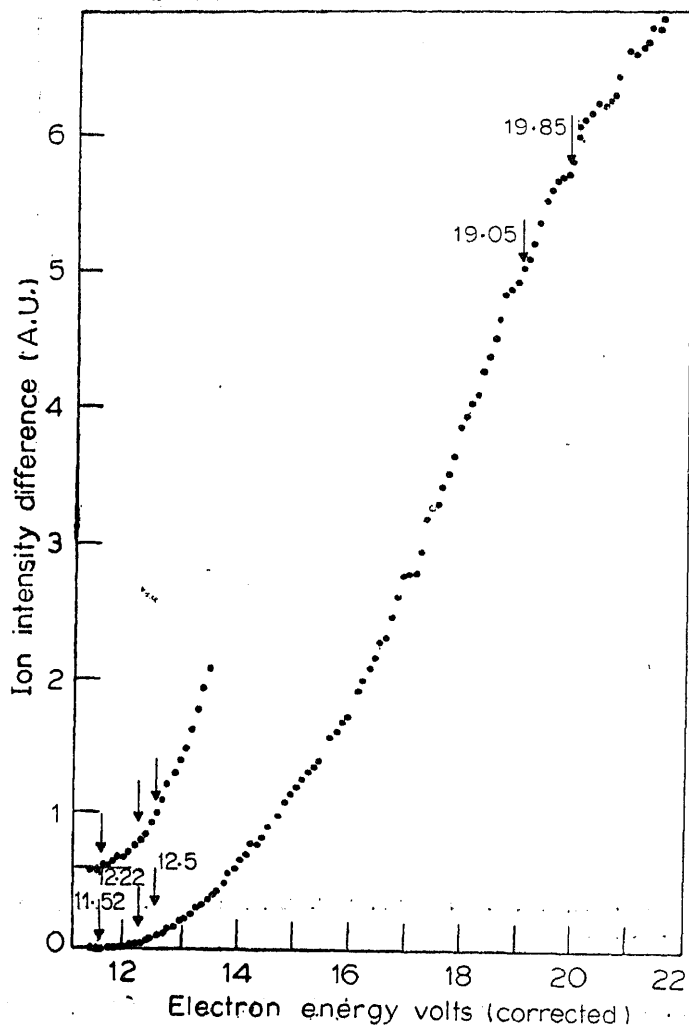


Figure 5. The ionization efficiency curve for fragment ion ($m/z = 55$) from *trans*-2-butene.

energy provided by steric conformation in the *cis*-isomer. However, one can argue that the value 0.79 eV is too a large value for the energy of steric conformation in the *cis*-isomer. Also, one may ask why similar energy of steric conformation does not appear in the fragmentation process leading to the formation of $C_4H_7^+$ fragment? The plausible explanation for the large difference between appearance energies obtained from the two isomers is that for unknown reason geometrical isomerism remains after the fragmentation of the two isomers and that the ground state of $C_4H_7^+$ fragment ion from *trans*-2-butene has a very low

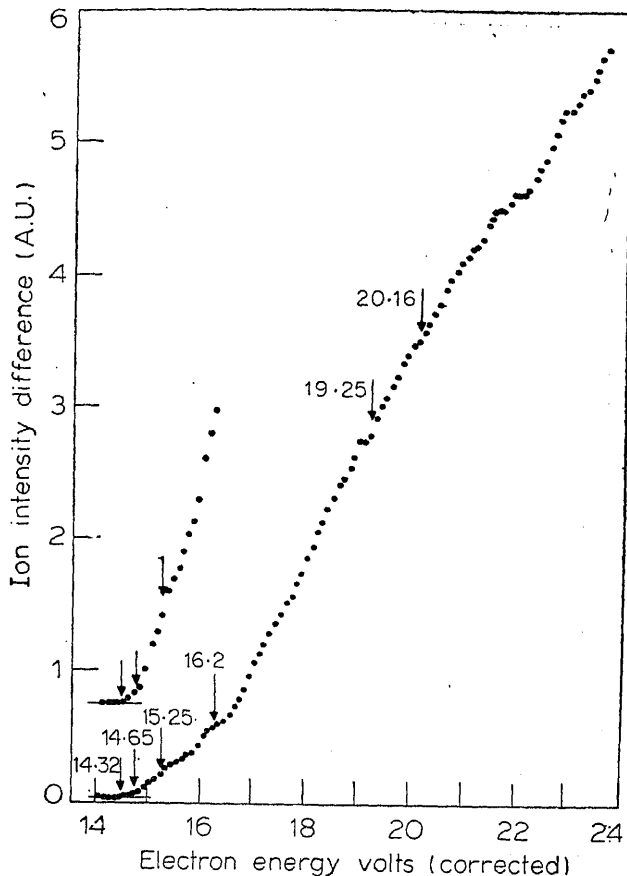
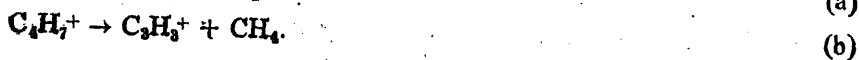


Figure 6. The ionization efficiency curve for fragment ion ($m/z = 39$) from *trans*-2-butene.

The structure in the IE curves of $C_3H_3^+$ fragments obtained from the two isomers are given in table 1. Three higher appearance energies appear at 19.57, 21.63, and 23.08 eV in the IE curve of $C_3H_3^+$ fragment produced from the *cis*-isomer but not in the IE curve of the fragment from the *trans*-isomer.

The $C_3H_3^+$ fragment ion is believed to be formed at the threshold from both isomers by the following processes having almost equal heats of formation :



Using charge transfer technique Sunner (1980) had detected two metastable peaks at m/z equal to 27.7 and 37.1 for the formation of $C_3H_3^+$ fragment from *cis*-2-butene. The first peak corresponds to the formation of $C_3H_3^+$ fragment from $C_3H_5^+$ fragment while the second peak corresponds to its formation from $C_4H_7^+$ fragment.

Table 1. Ionization and appearance energies for $C_4H_8^+$, $C_4H_7^+$ and $C_3H_3^+$ ions obtained from *cis*- and *trans*-2-butene.

Ion	Ionization and appearance energies			
	<i>cis</i> -butene		<i>trans</i> -butene	
	Present study	Previous work	Present study	Previous work
$C_4H_8^+$ ($m/z = 56$)	9.26 ± 0.06	$9.10^{(1)}$, $9.00^{(2)}$, $9.13 \pm 0.01^{(3)}$	9.25 ± 0.05	$9.10 \pm 0.15^{(1)}$ $9.13 \pm 0.01^{(3)}$
	9.55 ± 0.10		9.57 ± 0.07	
	10.00 ± 0.07		9.88 ± 0.05	
	10.53 ± 0.06		10.50 ± 0.09	
	15.35 ± 0.06		15.30 ± 0.10	
	17.90 ± 0.08		18.05 ± 0.10	
$C_4H_7^+$ ($m/z = 55$)	11.51 ± 0.08	$11.32^{(1)}$, $11.20^{(4)}$ $11.10 \pm 0.11^{(5)}$ $11.43 \pm 0.01^{(6)}$	11.52 ± 0.06	$11.24 \pm 0.1^{(5)}$
	12.13 ± 0.09		12.22 ± 0.10	
	..		12.50 ± 0.10	
	13.52 ± 0.07		..	
	18.95 ± 0.12		19.05 ± 0.12	
	19.95 ± 0.10		19.85 ± 0.12	
$C_3H_3^+$ ($m/z = 39$)	13.65 ± 0.09	$13.75^{(4)}$, $13.80 \pm 0.3^{(6)}$		
	14.12 ± 0.10		14.32 ± 0.08	$14.20 \pm 0.3^{(6)}$
	14.64 ± 0.05		14.65 ± 0.09	
	15.18 ± 0.09		15.25 ± 0.06	
	..		16.20 ± 0.06	
	19.19 ± 0.07		19.25 ± 0.07	
	19.57 ± 0.07		..	
	..		20.16 ± 0.10	
	21.63 ± 0.08		..	
	23.08 ± 0.08			

(1) Lossing 1972, (2) Meisels *et al* 1970, (3) Watarabe *et al* 1962, (4) Omura 1961, (5) Dibelar 1947, (6) Kramer and Dumbar 1973.

(process b). The mean value is equal to 279.4 kcal/mole which is in excellent agreement with ΔH_f value 281 kcal/mole for the propargyl ion $HC \equiv C^+CH_2$ reported by Lossing (1972). The presently reported ΔH_f value 279.4 kcal/mole is higher by about 23 kcal/mole than the heat of formation of $C_4H_8^+$ ion

Table 2. Ionization and appearance energy differences and heats of formation for $C_4H_8^+$, $C_4H_7^+$ and $C_3H_3^+$ ions obtained from *cis*- and *trans*-2-butene.

Ion	Ionization and appearance energy differences (eV) <i>Trans-cis</i>	ΔH_f (kcal/mol)	
		<i>Cis</i>	<i>Trans</i>
$C_4H_8^+$	-0.01	211.9	210.6
(<i>m/z</i> = 56)	0.02	218.6	218.0
	-0.12	..	..
	-0.03	..	..
	-0.05	..	..
	0.15	..	..
$C_4H_7^+$	0.01	211.7	210.9
(<i>m/z</i> = 55)	0.09	226.0	227.0
$C_3H_3^+$	..	279.4	..
(<i>m/z</i> = 39)	0.20	290.2	296.2

at the threshold. While the ΔH_f value for propargyl ion has not been established until now, the excellent agreement between the present result for this ion together with that of Lossing (1972) may indicate that ΔH_f for the ion is about 280 kcal/mole. Although, the processes (a and b) for formation of cyclopropenyl ion from *cis*-2-butene are multicenter dissociation processes which require reverse activation energy and probably also kinetic shift the presently reported value of ΔH_f for propargyl ion together with that calculated by Lossing (1972) may indicate that $C_3H_3^+$ is formed presently from *cis*-2-butene with almost zero excess energy.

The calculated ΔH_f value for the formation of $C_3H_3^+$ fragment from *trans*-2-butene according to process (a) is equal to 297.2 kcal/mole, while that value according to process (b) is equal to 296.1 kcal/mole. The mean value is equal to 296.6 kcal/mole and probably corresponds to the formation of $C_3H_3^+$ fragment with allenyl structure ($CH_2=C=CH^+$). The ΔH_f value for the formation of allenyl ion obtained from *i*-butene is calculated previously by Selim (1970) as 287.3 kcal/mole. It appears that the formation of $C_3H_3^+$ fragment from *trans*-2-butene needs more excess energy than the formation of the same ion from *i*-butene.

Finally, if one calculates the ΔH_f value for $C_3H_3^+$ fragment obtained from the *cis*-isomer corresponding to the second appearance energy (14.12 eV) the calculated value will be equal to 290.7 kcal/mole according to process (a) and 289.7 kcal/mole according to process (b). The mean value is equal to 290.2 kcal/mole

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Kinetics of $Tl(III)$ oxidation of hydroxylamine hydrochloride in aqueous sulphuric acid

VANGALUR S SRINIVASAN* and N VENKATASUBRAMANIAN
Vivekananda College, Mylapore, Madras 600 004, India

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Abstract. The kinetics of $Tl(III)$ oxidation of hydroxylamine hydrochloride $1.0\text{ M H}_2\text{SO}_4$ at a fixed chloride concentration has been investigated to make formal comparison of the observed rate with that of hydrazine sulphate. The reaction exhibits total second order kinetics—first order in each reactant. The rate of the reaction depends inversely on the first power of $[H^+]$ and $[Cl^-]$ suggesting the possible reactive species as $TlOH^{2+}$. To account for the stoichiometry of the reaction $[Tl(III)] : [H_2NOH.HCl] = 1.5 : 1$ and the products of the reaction HNO_2 and N_2O , two reaction schemes have been proposed.

Keywords. $Tl(III)$ - $H_2NOH.HCl$ reaction ; $TlOH^{2+}$ -active species ;
 $K_h = 3.3 \times 10^{-5} \text{ M}^2$

1. Introduction

Though the kinetics of $Tl(III)$ oxidation of hydrazine sulphate has been investigated in aqueous sulphuric acid by Srinivasan and Venkatasubramanian (1970, 1977), the kinetics of $Tl(III)$ oxidation of hydroxylamine has not been investigated so far. This paper has, therefore, been undertaken with a view to compare the reactivity towards these two similar reducing agents.

2. Results and discussion

2.1. Dependence of rate on $Tl(III)$ and $H_2NOH.HCl$ concentrations

The kinetics of $Tl(III)$ oxidation of hydroxylamine hydrochloride were studied in $1\text{ M H}_2\text{SO}_4$ at 30°C . From the rate dependence on the concentration of $Tl(III)$ and $H_2NOH.HCl$ (table 1) it has been found that the reaction exhibits total second order kinetics—first order with respect to $[Tl(III)]$ and first order with respect to $[H_2N.OH.HCl]$. As $Tl(III)$ is known to complex with Cl^- (Halverson *et al* 1956) total concentration of Cl^- has been adjusted to be 0.025 M by adding necessary amount of $NaCl$.

$[Ti(III)] M \times 10^3$ $[H_2NOH.HCl] M \times 10^2$ $k_2 \times 10^4$ litres
mole⁻¹ sec⁻¹

2.1	0.50	4.2
2.0	1.00	4.1
2.0	1.50	3.9
2.0	2.00	4.1
3.0	2.00	4.0
4.0	2.00	4.1

* Total chloride ion concentration is kept at 0.025 M by adding required amount of NaCl in each case.

2.2. Dependence on acid concentration

The reaction rate is decreased by increasing sulphuric acid concentration from 0.50 M to 2.0 M only (table 2). The plot of $\log k_2$ versus $\log [\text{acid}]$ is linear with a slope equal to -1 and this is similar to what was observed in the $Ti(III)$ oxidation of hydrazine sulphate (Srinivasan and Venkatasubramanian 1970).

2.3. Effect of added chloride ions

With increasing concentration of chloride ions rate decreases (table 3) and a plot of $\log k_2$ versus $\log [Cl^-]$ is linear with a slope very nearly equal to -1 .

2.4. Temperature influence

The effect of temperature on the reaction rate was studied between 30° and 50° C (table 4) and from the plot of $\log k_2$ versus $1/T$, energy of activation has been calculated. The thermodynamic parameters derived therefrom are summarised in table 4.

2.5. A comparative rate picture of hydrazine and hydroxylamine $k_2 \times 10^2$ (N_2H_4) = 52 litre mole⁻¹ sec⁻¹ and $k_2 \times 10^2$ ($NH_2OH.HCl$) = 0.158 l mole⁻¹ sec⁻¹ at 30° C under identical conditions) clearly indicates that hydroxylamine gets oxidised about 3.5×10^2 times slower than hydrazine sulphate. This is probably due to the lower reducing property of hydroxylamine wherein the removal of hydrogen from nitrogen may be difficult due to the $-I$ effect of the $-OH$ group attached to the nitrogen.

3. Mechanism of the oxidation of hydroxylamine by $Ti(III)$

3.1. Nature of active $Ti(III)$ species

In the presence of added chloride ion, $Ti(III)$ forms a complex, $TiCl^{2+}$, which may get hydrolysed under the reaction conditions, according to the equilibrium

$[\text{H}_2\text{SO}_4] \text{ M}$ $k_2 \times 10^3 \text{ litres}$
 $\text{mole}^{-1} \text{ sec}^{-1}$

0.50	7.1
1.00	4.2
1.50	3.2
2.00	1.86

* Total ionic strength is maintained at 2.0 by adding suitable amount of KHSO_4 .

Table 3. Effect of added chloride ion on the rate of oxidation.

$[\text{H}_2\text{NOH} \cdot \text{HCl}] = 5.0 \times 10^{-3} \text{ M}$; $[\text{H}_2\text{SO}_4] = 1.0 \text{ M}$;
 $[\text{Ti(III)}] = 2.0 \times 10^{-3} \text{ M}$; $[\text{Na}_2\text{SO}_4] = 0.20 \text{ M}$; Temp.: 30° C

$10^3 \times [\text{Cl}^-] \text{ M}$	$k_2 \times 10^4 \text{ litres}$ $\text{mole}^{-1} \text{ sec}^{-1}$
5.0	15.8
10.0	6.7
20	4.0
25	2.0

Table 4. Temperature dependence and thermodynamic parameters.

$[\text{H}_2\text{NOH} \cdot \text{HCl}] = 5.0 \times 10^{-3} \text{ M}$; $[\text{H}_2\text{SO}_4] = 1.0 \text{ M}$; $[\text{Ti(III)}] = 2.0 \times 10^{-3} \text{ M}$;
 $[\text{Na}_2\text{SO}_4] = 0.20 \text{ M}$

$k_2 \times 10^3 \text{ litres mole}^{-1} \text{ sec}^{-1}$	30 °C	40 °C	50 °C
	1.60	5.1	36
E_a kcal/mole	30		
$\Delta H^\ddagger$ kcal/mole	29		
$\Delta S^\ddagger$ cal/mole/deg	+25		



The hydrolytic constant,

$$K_h = \frac{[\text{TiOH}^{2+}] [\text{H}^+] [\text{Cl}^-]}{[\text{TiCl}^{3+}]}$$

Therefore,

$$[\text{TiOH}^{2+}] = \frac{K_h [\text{TiCl}^{2+}]}{[\text{H}^+] [\text{Cl}^-]}$$

Under the reaction conditions, the observed inverse first order dependence $[\text{H}^+]$ and $[\text{Cl}^-]$, suggests the probable reactive species as TiOH^{2+} .

From the rate expression,

$$-\frac{d[\text{Ti(III)}]}{dt} = k_{\text{obs}} [\text{Ti(III)}] [\text{H}_2\text{NOH.HCl}]$$

it follows that

$$-\frac{d[\text{Ti(III)}]}{dt} = k_2 \frac{K_h [\text{TiCl}^{2+}]}{[\text{H}^+] [\text{Cl}^-]} [\text{Hydroxylamine hydrochloride}]$$

whence

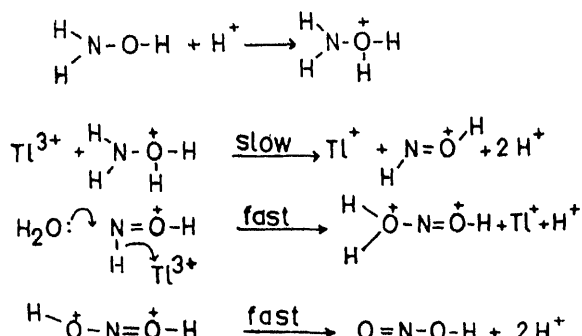
$$k_{\text{obs}} = \frac{k_2 K_h [\text{TiCl}^{2+}]}{[\text{H}^+] [\text{Cl}^-]}$$

It follows from (6) that a plot of k_{obs} versus $1/[\text{Cl}^-]$ should be linear, a given $[\text{H}^+]$, passing through the origin, with the slope equal to $k_2 K_h/[\text{H}^+]$ where k_2 is the specific rate, in the absence of Cl^- , obtained by extrapolation method. From the slope, K_h , evaluated comes to $3.3 \times 10^{-5} \text{ M}^2$ which is very close to hydrolytic constant reported for TiCl^{2+} (Basolo and Pearson 1967).

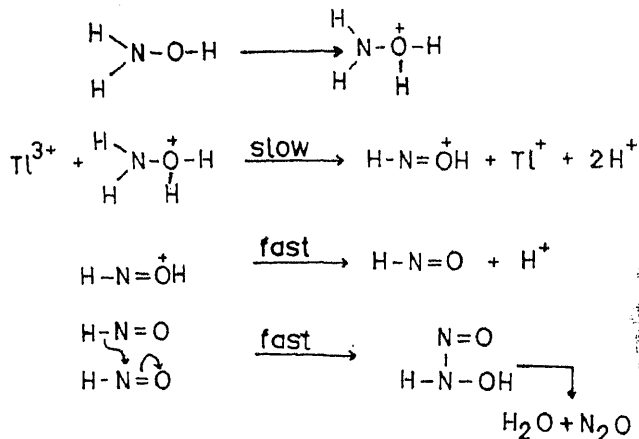
3.2. The oxidation products, in the hydroxylamine— Ti(III) reaction, are Ti(IV) and HNO_2 (Wiberg 1965) and the reaction has stoichiometry of $[\text{Ti(III)}] : [\text{H}_2\text{NOH.HCl}] = 1.5 : 1$. A mechanism consistent with the experimentally observed rate-law

$$-\frac{d[\text{Ti(III)}]}{dt} = k_2 [\text{Ti(III)}] [\text{H}_2\text{NOH.HCl}]$$

could be the following :



According to scheme 1, $[Ti(III)] : [Hydroxylamine] = 2 : 1$. The formation of N_2O on the other hand may be picturised as follows :



SCHEME II

The stoichiometry according to scheme 2 is 1 : 1. As the experimentally observed stoichiometry is $[Ti(III)] : [H_2NOH \cdot HCl] = 1.5 : 1$, it will be consistent with both the above schemes. Since the products of the reaction are also reducing agents, there may be more uptake of oxidant during stoichiometric studies and hence stoichiometry tended to vary with time and acidity of the medium.

4. Experimental

Thallic oxide (BDH) was used as such and this had 99% purity as evidenced by iodometric estimation of its solution in sulphuric acid. Sulphuric acid was standardised after suitable dilution using standard carbonate free, NaOH solution. Hydroxylamine hydrochloride (BDH) was used after two recrystallisations. The course of the reaction was followed by pipetting out 5 ml aliquots of the reaction mixture at various intervals and quenching in iodate free KI solution and estimating the iodine liberated using standard thiosulphate to a starch end point. The specific rate (k_2) has been evaluated using the integrated rate equation and velocity constants are reproducible within $\pm 5\%$.

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Mössbauer studies on ferrous-zinc ferrites prepared by a novel technique*

C E DESHPANDE, S K DATE, M P GUPTA and
M N S MURTHY†

Physical Chemistry Division, National Chemical Laboratory, Pune 411 008, India

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Abstract. Ferrous-zinc ferrites, $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ ($0 < x < 1$) have been prepared using a new method involving the stabilization of FeO prior to its reaction with ZnO and Fe_3O_4 . Mössbauer studies on these ferrites have given results regarding the hyperfine fields, quadrupole interactions and isomer shifts in good agreement with those reported earlier on the same ferrites prepared by more elaborate and expensive techniques. This confirms the reliability of the new technique, which being much simpler, is less prone to errors in stoichiometry.

Keywords. Ferrous-zinc ferrites; Fe_3O_4 ; Mössbauer studies.

1. Introduction

Ferrous-zinc ferrites have large values of saturation magnetization and therefore are capable of application in recording heads and transformer-core materials. They have not been industrially exploited however since their preparation is difficult (Stuijts *et al* 1971) because of the need for the existence of large and specific amounts of the highly oxidizable and unstable Fe^{2+} in them. It is obviously not possible to start with the required amount of FeO (along with the other oxides) since FeO not only oxidizes spontaneously in air but even disproportionates in vacuum to Fe_3O_4 and Fe. Elaborate and indirect methods have therefore been used for the preparation of these ferrites. Stuijts *et al* (1971) and Srivastava *et al* (1976 p. 2032) have thermally reduced a mixture of ZnO and Fe_2O_3 to the required extent in a special furnace and in a flowing current of nitrogen. They followed the extent of reduction of Fe^{3+} to Fe^{2+} in the reacting powders by an analysis of the incoming and outgoing gases. Dobson *et al* (1970) have heated Fe_2O_3 and ZnO

a reduction of Fe^{3+} to Fe^{2+} by metallic iron. It may become difficult in such a method to get the resulting compound with the same homogeneity and stoichiometry as from a simple solid state reaction among metal oxides involving no change of valency in the process.

Two of the present authors (Deshpande and Murthy 1981) have reported earlier a novel and accurate method of preparing ferrous-zinc ferrites without difficulty. Highly active ferric oxide prepared at a low temperature (Murthy *et al* 1979) was heated at 950°C for 8 hr in the presence of (but out of physical contact with) an excess of reduced iron in a gas-tight silica furnace-tube filled with pure nitrogen and provided with a manometer-*cum*-mercury seal to release any pressure developed during the heating. The iron acted as an oxygen-getter and reduced the Fe_2O_3 to a compound $\text{Fe}_{(1-\delta)}\text{O}$ where δ estimated by chemical analysis was less than 0.1. This material containing mostly FeO and a very small amount of Fe_2O_3 was quite stable in air. Calculated quantities of Fe_2O_3 and ZnO were then mixed with a known weight of the above reduced analysed oxide of iron, and reacted at $1000^\circ\text{C}/12\text{ hr}$ in a static inert atmosphere under reduced pressure. The initial low pressure of nitrogen in the unit prevented any bubbling out of gases and consequent loss of oxygen on heating, through the mercury cut-off-*cum*-manometer assembly. The resulting ferrite powder on cooling always analysed to the required composition within the usual limits of accuracy of chemical analysis. The preparation of ferrous-zinc ferrites thus became a straightforward one involving a usual solid state reaction between analysed oxides; and any required composition could be easily reproduced accurately since there was no need to change the valency of iron during the reaction. The resulting powder was pressed with a volatilizable binder such as camphor, polymethyl methacrylate or polyamine sulphones. The binder was then distilled off in a current of oxygen-free nitrogen and the pieces were sintered at $1270^\circ\text{C}/8\text{ hr}$ in a static nitrogen atmosphere under reduced pressure (so that no gases could bubble out on heating). The sintering unit is given in another earlier paper (Murthy *et al* 1979). The cubic lattice parameters and some magnetic measurements on the sintered ferrous-zinc ferrites $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ with $x = 0.2, 0.3, 0.4, 0.5$ and 0.6 have been reported in the earlier paper (Deshpande and Murthy 1981). We report in this paper some Mössbauer studies on the ferrous-zinc ferrites prepared by this method.

2. Experimental

2.1. Preparation of the compounds

The compounds $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ with $x = 0.2, 0.4, 0.6$ and 0.8 were prepared by the method outlined in the introduction and reported earlier (Deshpande and Murthy 1981). The compound with $x = 0$ *i.e.* Fe_3O_4 was prepared by a solid state reaction between calculated quantities of Fe_2O_3 and the analysed compound $\text{Fe}_{(1-\delta)}\text{O}$ ($\delta < 0.1$) referred to earlier in the introduction. This reaction was carried out under the same conditions as those used for the other compounds $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ with $0 < x \leq 1$. The compound with $x = 1$ *i.e.* ZnFe_2O_4

ment between the expected and analysed compositions of $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ within the usual limits of accuracy of volumetric analysis. X-ray diffraction studies with Philips pw 1730 x-ray generator using $\text{Fe K}\alpha$ radiation indicated a single phase in each case with cubic lattice parameters varying linearly with x . The initial permeability (μ_i) and the quality factor (Q) at 800 kHz were measured on sintered toroids (2 cm O.D., 1 cm I.D. and 0.5 cm thickness) with Hewlett Packard 4342 A Q-meter. All these data are given in table 1.

2.2. Mössbauer experiments

Mössbauer spectra were recorded with a conventional constant acceleration electromechanical drive coupled to ND 100 multichannel analyser operating in time mode. A 5 mCi ^{57}Co : Rh source was used to record the spectra at room temperature. A metallic iron foil (25 μ) was used to calibrate the spectrometer and all isomer shifts were measured with respect to that of metallic iron. All the hyperfine (hf) interaction parameters were computed using an iterative least squares MOSFIT program on ICL 1409 computer.

3. Results and discussion

Figure 1 shows the typical Mössbauer spectra recorded at room temperature for various compositions of $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ where $x = 0$ (i.e. Fe_3O_4), 0.2, 0.4, 0.6, 0.8 and 1.0 (i.e. ZnFe_2O_4). Figure 1a clearly shows the hyperfine (hf) split spectrum with characteristic parameters attributable to Fe_3O_4 . These parameters are $H_n(A) = 485 \pm 5$ kOe, $H_n(B) = 453 \pm 5$ kOe, $\Delta E_q(A) = 0.10 \pm 0.04$ mm/sec, $\Delta E_q(B) = -0.08 \pm 0.04$ mm/sec., $IS(A) = 0.36 \pm 0.02$ mm/sec, $IS(B) = 0.75 \pm 0.02$ mm/sec. These values are in excellent agreement with those reported earlier in the literature (MEDI 1974); and are particularly significant since the Fe_3O_4 was prepared by a new method which was exactly similar to the one used for preparing ferrous-zinc ferrites also.

Mössbauer spectra figures 1(b) to 1(f)—for the various compositions of $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ show the effect of dilution with zinc on the hyperfine field experienced by the iron ions at the tetrahedral and the octahedral sites. It is well-known that the Zn^{2+} ions occupy the tetrahedral sites in spinel ferrites and are therefore expected to decrease the hf field at these sites. However the decrease in hf field is also observed for the iron ions at the octahedral sites. Due to the zinc substitution it seems that the cation distribution ($\text{Fe}^{2+}/\text{Fe}^{3+}$) has effectively altered, reflecting the decrease in the hf field. For all the compositions except $x = 0.8$, hf parameters have been computed and given in table 2. For $x = 0.6$, strong broad absorption wings extending over to ~ 4 mm/sec in the centre of the spectrum are observed. These results agree qualitatively with those reported earlier by Dobson *et al* (1970) and Srivastava *et al* (1976, p. 2041) although the method of

Table 1. xrd, chemical analysis and magnetic measurements on $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$.

X	Cubic lattice parameter 'a', $\pm 0.005 \text{ \AA}$	Fe^{2+}/g		Total Fe/g		μ_4 at 800 kHz	Q at 800 kHz	μQ
		Anal.	Cal.	Anal.	Cal.			
0.0	8.393	0.2380	0.2412	0.7240	0.7236	...	...	...
0.2	8.405	0.1938	0.1913	0.6752	0.6698	75.96	30.5	2316.78
0.4	8.416	0.1448	0.1447	0.6201	0.6169	165.00	17.5	2887.50
0.6	8.430	0.0946	0.0941	0.5679	0.5649	298.00	5.75	1713.50
0.8	8.439	0.0470	0.0467	0.5141	0.5137	...	...	...
1.0	8.450	0.0000	0.0000	0.4653	0.4633	...	...	...

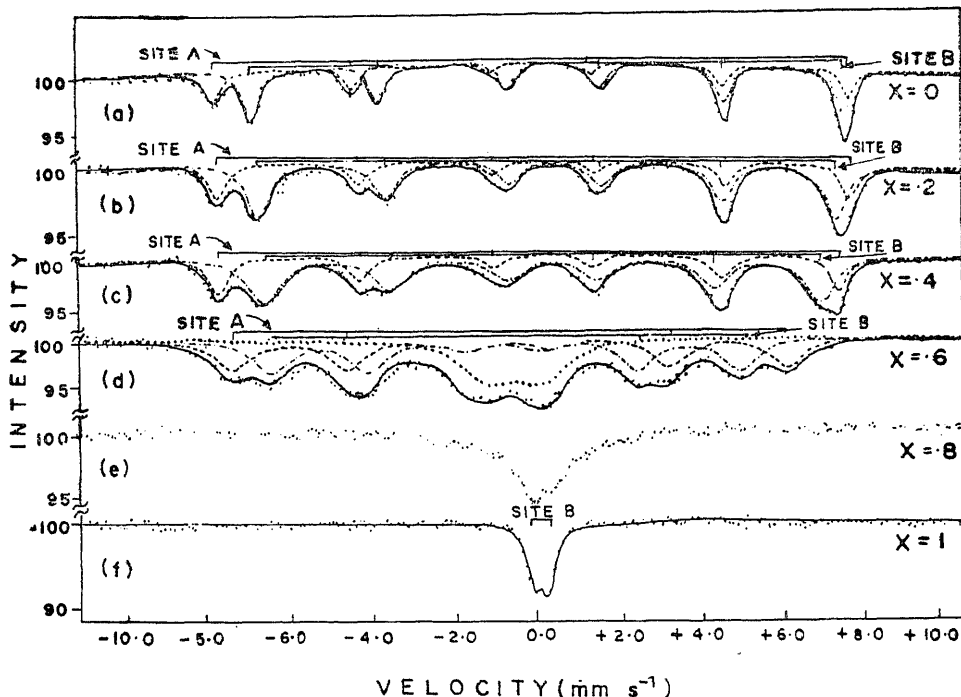


Figure 1. Mössbauer spectra of $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ at room temperature ;
 (a) $x = 0.0$ (b) $x = 0.2$, (c) $x = 0.4$, (d) $x = 0.6$, (e) $x = 0.8$, (f) $x = 1.0$.

Table 2. Mössbauer data on $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$

Sl. No.	x	Pattern	$iS \pm 0.02$ mm/sec w.r.t. iron metal	$E_Q \pm 0.04$ mm/sec.	$H_n \pm 5 \text{ kOe}$
1.	0	A	0.36	0.1	485
		B	0.75	-0.08	453
2.	0.2	A	0.40	0.14	480
		B	0.75	0.08	440
3.	0.4	A	0.40	0.21	464
		B	0.71	0.15	414
4.	0.6	A	0.49	0.08	420
		B	0.62	0.09	350
		C	Central doublet contribution present.		
5.	0.8	Complex non-lorentzian spectrum.			

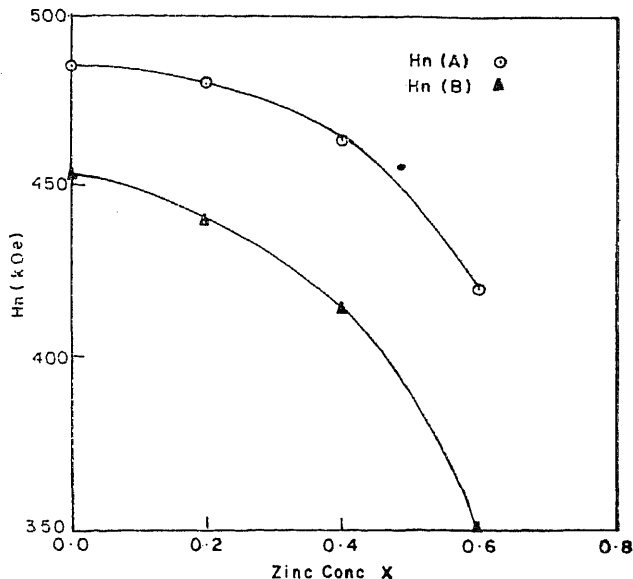


Figure 2. Hyperfine fields, H_n (kOe) corresponding to (A) and (B) sites vs x in $\text{Zn}_2\text{Fe}_{3-x}\text{O}_4$.

preparation of ferrite samples is totally different. For the zinc concentration of $x = 0.8$ [figure 1 (e)] the Mössbauer spectrum is a broad non-Lorentzian, showing either the hf field distribution effects and/or electron spin relaxation effects. It is difficult to differentiate the contributions from these two effects and therefore no attempt is made to compute hf interaction parameters.

In figure 2 we have plotted $H_n(A)$ and $H_n(B)$ vs the amount of zinc substituted in ferrite samples. It is seen clearly that the fields at (A) and (B) sites decrease regularly with increase in zinc concentration. At $x = 0.6$ the hyperfine fields at both the sites, (A) and (B), have decreased appreciably. We have not computed any hf interaction parameters in the concentration range $0.6 < x < 0.8$ due to the unresolved broad hyperfine structure. For the zinc concentration of $x = 1.0$ the Mössbauer spectrum as expected is very simple showing only the quadrupole split partners. The hf parameters are $\Delta E_q = 0.34 \pm 0.04$ mm/sec. and $IS = 0.49 \pm 0.04$ mm/sec. exhibiting the unique octahedral site of Fe^{3+} in zinc ferrite. All our results agree very well with those of Dobson *et al* (1970) and Srivastava *et al* (1976, p. 2041) except for the compound $\text{Zn}_{0.4}\text{Fe}_{2.6}\text{O}_4$ (corresponding to $x = 0.4$) in the latter paper.

4. Conclusion

Mössbauer spectra of $\text{Zn}_2\text{Fe}_{3-x}\text{O}_4$ with $0 < x < 1$ prepared by a new and simple technique using a stabilized oxide of iron very rich in FeO, indicate that hyper-

a stabilized FeO is very convenient, reliable and reproducible.

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Chemical shifts of the x-ray K or L_{III} absorption edges

K S SRIVASTAVA[†], M HUSAIN, KIRTI SINHA, PRATIBHA GUPTA, A K SRIVASTAVA, V KUMAR* and SHIV SINGH**

Theoretical Physics Division, Physics Department, Lucknow University,
Lucknow 226 007, India

* Department of Maths and Physics, Indian School of Mines, Dhanbad (Bihar), India

** On leave from Physics Department, Hindu College, Moradabad.

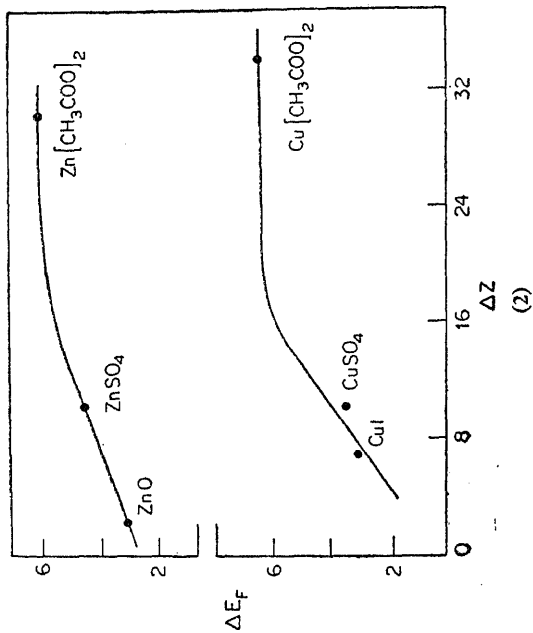
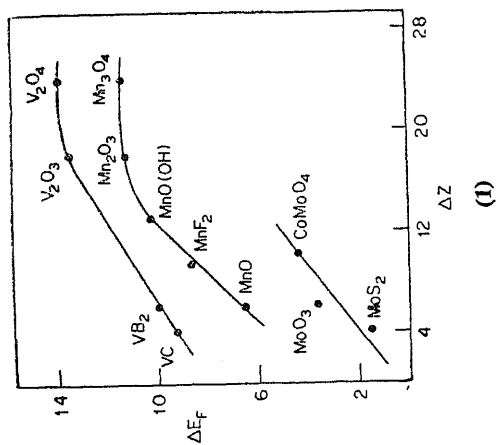
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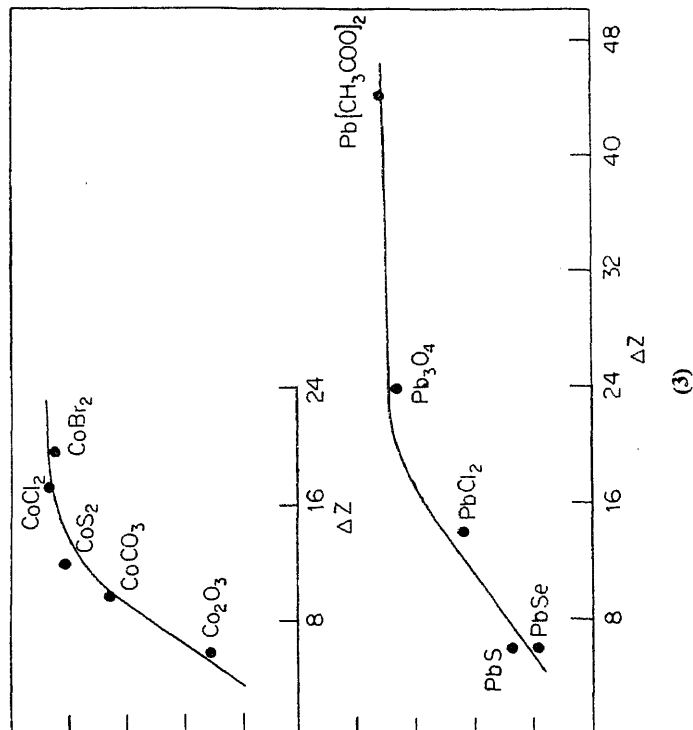
Abstract. The x-ray K or L-absorption edge shifts of V, Mn, Mo, Zn, Cu, Co, Pb, Ga, Fe and Y, when they undergo chemical combination and form compounds, have been calculated. It has been found that the major contribution to the chemical shift comes from the change in the Fermi energy of a metal when it forms a compound. The calculated values for the change in Fermi energy correspond well with the values observed by several workers for the chemical shift.

Keywords. Chemical shifts; x-ray absorption edges.

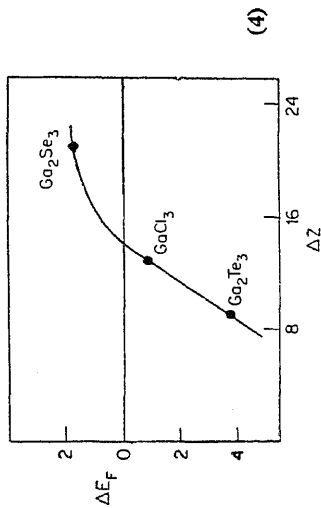
In recent years great interest has been shown in giving various possible explanations for the experimentally observed chemical shifts in x-ray absorption edges. Attempts have been made to correlate chemical shift empirically with the ionic or covalent character of the bond, valency, hybridization and electronegativity, etc. (Agarwal and Verma 1970; Dey and Agarwal 1971; Bhide and Bahl 1972; Kawata and Maeda 1978). Recently Salem *et al* 1978 have reported that the chemical shift of K-absorption edge of vanadium in some of its compounds is due to effective ionic charge. But none of the authors mentioned above have been able to give the numerical order or nature (*i.e.*, sign of the shift) of the observed chemical shift.

A survey of the literature shows that the problem of correlating the experimentally observed x-ray absorption edge shifts with the calculated value of the chemical shift requires a more systematic investigation. Many workers believe that the change in the chemical environment of a metal, when it forms a compound is due to redistribution of electronic charge in particular orbitals (Seigbahn *et al* 1967; Lindberg *et al* 1970; Vishnoi 1970; Pendharkar and Mande 1973). This indicates that Fermi level should change because of redistribution of charge in the

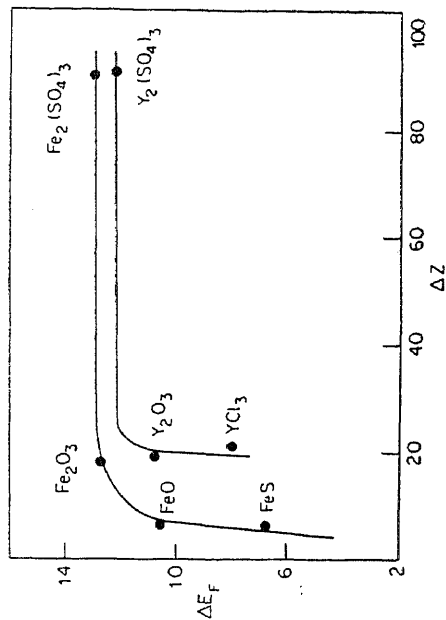




(3)



(4)



(5)

Figures 1-5. Plot of Fermi energy shift ($\Delta E_F = \Delta E_c$) versus change in effective number of electrons (ΔZ).

out that the Fermi energy of a metal changes when it undergoes a chemical combination and forms a compound. The authors have used this method (Srivastava *et al* 1979) recently for Pb and Bi. We also know that K or L- edge in an x-ray absorption spectrum corresponds to a transition of an electron from the corresponding core level to the first unoccupied vacancy in or above the Fermi surface. Thus, if the Fermi surface of a metal changes on chemical combination, its absorption edge will also change. Blokhin (1961) has used Sommerfeld expression for the Fermi energy as

$$E_F = \frac{h^2}{8m} \left[\frac{3n}{\pi} \right]^{2/3} \quad (1)$$

Differentiating this, we get

$$\begin{aligned} \Delta E_F &= \left[\frac{h^2}{12m} \left(\frac{3}{\pi} \right)^{2/3} n^{-1/3} \right] \Delta n \\ &= \text{constant } \Delta n. \end{aligned} \quad (2)$$

This change in Fermi energy should correspond to the chemical shift. Thus

$$\begin{aligned} \Delta E_F &= \Delta E_C = \text{constant } \Delta n \\ &= \text{constant } \Delta Z. \end{aligned} \quad (3)$$

Thus chemical shift varies linearly with the change in the number of electrons (ΔZ) in the Fermi surface. A plot of ΔE_F versus ΔZ for V, Mn, Mo, Zn, Cu, Co, Pb, Ga, Fe and Y metals and their compounds have been shown in figures 1 to 5. It has been found that ΔE_F varies linearly with ΔZ upto $\Delta Z = 20$. Sapre and Mande 1973 have also observed linear variation of chemical shift with q_p upto $q_p = 1.3$. In order to get the numerical value of E_F one can express equation (1) in terms of plasmon energy as

$$E_F = 0.29484 (\hbar\omega_p)^{4/3} \text{ eV} \quad (4)$$

where

$$\hbar\omega_p = 28.8 \left(\frac{Z\sigma}{W} \right)^{1/2} \text{ eV}. \quad (5)$$

Z is the effective number of electrons taking part in plasma oscillations, σ is the specific gravity and W is the molecular weight.

The expression for $\hbar\omega_p$ given in equation (5) is valid for the free electron gas model but to a first approximation can be used for dielectrics too (Srivastava *et al* 1979).

According to Kittel (1977) plasma oscillations in dielectrics are physically the same as in metals. This fact can be substantiated from the work of Raether (1965) and Philipp and Ehrenreich (1963) who have shown that the plasmon frequency for dielectrics is

Metal/ compound	$Z^{a,b}$	Calculated ΔE_F in eV	Experimental C.S. ΔE_g in eV
V	1	...	...
VC	5	9.24	9.38 ± 0.47^a
VB ₂	7	9.99	6.82 ± 0.42^a
V ₂ O ₃	20	13.30	10.75 ± 0.40^a
V ₂ O ₄	26	13.90	12.41 ± 0.47^a
Mn	1	...	...
MnO	7	6.58	5.4^a
MnF ₂	10.6	8.66	7.57 ± 0.52^a
MnO (OH)	14	10.09	11.75^f
Mn ₂ O ₃	20	11.18	12.45^f
Mn ₃ O ₄	27	11.24	10.20^g
Mo	1	...	...
MoS ₂	5	1.57	2.4^h
MoO ₃	7	3.68	2.8^h
CaMoO ₄	11	4.30	3.4^h
Zn	1	...	...
ZnO	3	3.14	3.0 ± 0.3^i
ZnSO ₄	11	4.52	5.35 ± 0.3^i
Zn(CH ₃ COO) ₂	31	5.99	4.37 ± 0.3^i
Cu	1	...	...
CuI	8	2.91	2.20 ± 0.6^j
CuSO ₄	11	3.25	4.88 ± 0.6^j
Cu (CH ₃ COO) ₂	35	6.43	9.72 ± 0.6^j
Co	1	...	...
CoS	7	7.1972	7.41 ± 1.0^k
CoSe	7	7.3175	3.99 ± 1.0^k
Co ₂ O ₃	8	2.94	2.20 ± 0.3^l
CoCO ₃	11	6.33	7.34 ± 0.3^l
CoS ₂	13	7.92	8.99 ± 1.0^k
CoCl ₂	18.4	8.48	7.2^m
CoBr ₂	20.8	8.28	8.6 ± 0.3^n
Pb	4	...	...
PbSe	10	1.8	2.7 ± 0.7^o
PbS	10	2.59	4.0 ± 0.7^p
PbO	10	5.35	3.2 ± 0.7^p

Table 1. (Contd.)

Metal/ Compound	$Z^{a,b}$	Calculated ΔE_F in eV	Experimental C.S. ΔE_c in eV
PbCl ₂	18	4.2	3.0 ± 0.7 ^p
Pb ₃ O ₄	36	6.5	4.5 ^q
Pb(CH ₃ COO) ₂	50	6.99	5.2 ^q
Ga	3	...	...
Ga ₂ Tl ₃	12	-3.83	-3.4 ± 0.5 ^r
GaCl ₃	15.9	-0.87	-0.81 ± 0.5 ^s
Ga ₂ Se ₃	24	1.57	1.3 ± 0.5 ^r
Fe	1	...	...
FeS	7	6.74	6.5 ^t
FeO	7	10.54	9.2 ^d
Fe ₂ O ₃	20	12.61	12.1 ^d
Fe ₂ (SO ₄) ₃	92	13.72	13.9 ^d
Y	1	...	...
YCl ₃	22	7.98	9.85 ^u
Y ₂ O ₃	20	10.72	7.5 ^u
Y ₂ (SO ₄) ₃	92	12.26	13.14 ^u

a. (Srivastava *et al* 1979)c. (Salem *et al* 1978)e. (Salem *et al J. Phys.* 1978)g. (Padalia *et al* 1973)

i. (Gupta and Nigam 1972)

k. (Kondawar and Mande 1976)

m. (Kondawar and Mande 1973)

o. (Vishnoi and Agarwal 1970)

q. (Vishnoi 1970)

s. (Verma and Agarwal 1967)

u. (Bhide and Bhat 1968).

b. (Srivastava and Kumar 1981)

d. (Sanner 1941)

f. (Kulkarni and Mande 1971)

h. (Kawata and Maeda 1973)

j. (Verma and Agarwal 1968)

l. (Nigam and Gupta 1973)

n. (Dey and Agarwal 1972)

p. (Dey and Agarwal 1971)

r. (Sapre and Mande 1973)

t. (Lindh 1925)

where $\delta\epsilon_0$ is a very small quantity and can be neglected to a first approximation. Philipp and Ehrenreich (1963) have shown that the calculated values of $\hbar\omega_{ps}$ and $\hbar\omega_p$ are in fair agreement with their observed value of plasmon energy for dielectrics.

With the help of equation (4) the difference ΔE_F in the Fermi energy of a metal and its compounds has been calculated. It has been found that ΔE_F agrees

explains the nature of chemical shift. On these lines one can correlate the chemical shift data and make predictions regarding the nature of the chemical shifts in various compounds of a metal with the help of their Fermi energies only. In case of some compounds the difference between our theoretical values and experimentally observed values may be due to the fact that (i) we have used an approximate but simple method for calculating Fermi energies ' E_F ' and we have not taken into account the effect of relaxation energy, screening effect, etc. as their contribution to chemical shift is small and complexities are involved for their calculations. (ii) experimental values of ΔE_c for the same compounds by different workers (Lindh 1925; Sanner 1941; Kulkarni and Mande 1971; Gupta and Nigam 1972; Saxena *et al* 1974; Salem *et al* 1978) vary as much as up to 40%. Thus within the limits of experimental errors and theoretical approximations the calculated values of ΔE_c and ΔE_F are in fair agreement with each other.

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Isentropic compressibilities of ternary systems with 1-alkanol as non-common component

G RAJENDRA NAIDU and P R NAIDU

Chemical Laboratories, College of Engineering, Sri Venkateswara University,
Tirupati 517 502, India

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Abstract. New isentropic compressibility data are reported for four ternary mixtures, which contained methylethylketone and *n*-octane as common components. 1-propanol, 1-butanol, 1-pentanol and 1-hexanol, which form a homologous series, were used as non-common components. The deviation in isentropic compressibility has been computed from the experimental results and compressibility of ideal mixtures. The deviation is positive over the whole range of volume fraction in the four mixtures. The positive deviation suggests that the structure breaking effect of the components outweighs the structure making effect.

Keywords. Isentropic compressibility; interferometer; molar volume; excess volume; volume fraction; sound velocity.

1. Introduction

We report here isentropic compressibilities for four ternary systems: methylethylketone(1) + 1-alkanol(2) + *n*-octane(3) at 303.15 K. This is in continuation of our earlier work (Naidu and Naidu 1981) on isentropic compressibilities of ternary mixtures which contained *n*-heptane as one of the components. The alkanols used here include: 1-propanol, 1-butanol, 1-pentanol and 1-hexanol. While *n*-octane is capable of exerting structure breaking effect on self-associated alkanols, methylethylketone would be able to exert both structure breaking and structure making effects. Hence, the systems afford an opportunity to study the relative strengths of structure breaking and structure making of the common components. Further, the data included here are expected to throw light on the effect of *n*-alkane chain length on isentropic compressibility.

2. Experimental

The alcohols (BDH) were purified by the method described earlier (Rao and Naidu 1974). Methylethylketone (BDH) was purified by the method described earlier.

Table 1. Densities of pure substances at 303.15 K.

Liquid	Present work $\rho/\text{g cm}^{-3}$	Literature $\rho/\text{g cm}^{-3}$
1-Propanol	0.79562	0.79567
1-Butanol	0.80202	0.80206
1-Pentanol	0.80762	0.80764
1-Hexanol	0.81198	0.81201
<i>n</i> -Octane	0.69445	0.69450
Methylethylketone	0.79449	0.79452

Table 2. Sound velocities and isentropic compressibilities of pure liquids at 303.15 K.

Liquid	u (ms^{-1})	K_s (TPa^{-1})
1-Propanol	1190	888
1-Butanol	1224	832
1-Pentanol	1257	784
1-Hexanol	1285	746
<i>n</i> -Octane	1148	1093
Methylethylketone	1170	920

(Reddy and Naidu 1977). *n*-Octane (Riedel) was dried over sodium and then fractionally distilled. The purities of the samples were checked by comparing the measured densities with those reported in the literature (Timmermans 1950). The numerical data are given in table 1. Densities were measured using a bicapillary pycnometer described earlier (Rao 1974).

Isentropic compressibilities were computed from ultrasonic sound velocity and density using the relation

$$K_{s123} = u^{-2} \rho^{-1} \quad (1)$$

where K_{s123} , u and ρ denote isentropic compressibility, sound velocity and density respectively of a ternary mixture. The values of K_{s123} were accurate to ± 2 TPa. Ultrasonic sound velocities were measured with a single crystal ultrasonic interferometer at a frequency of 2 MHz and the values were accurate to $\pm 0.15\%$. Further, sound velocities were measured at a constant temperature, 303.15 ± 0.01 K. The densities for ternary mixtures were calculated from the experimental V^E included in our earlier communication (Naidu and Naidu 1982). The

Table 3. Experimental values for the isentropic compressibilities of ternary mixtures at 303.15 K.

Volume fraction of mek ϕ_1	Volume fraction of 1-alkanol ϕ_2	ρ (g cm ⁻³)	u (ms ⁻¹)	K_{s123} (TPa ⁻¹)	K_{s123} (TPa ⁻¹)
Methylethylketone (1) + 1-propanol (2) + <i>n</i> -octane (3)					
0.7029	0.1145	0.77378	1163	956	8
0.5860	0.2206	0.77314	1164	955	9
0.5971	0.2356	0.77609	1168	945	4
0.4794	0.2991	0.77029	1165	957	8
0.4394	0.3335	0.76975	1169	951	3
0.3348	0.4860	0.77534	1173	937	2
0.3055	0.4780	0.77124	1172	944	2
0.2092	0.6196	0.77650	1175	933	4
Methylethylketone (1) + 1-butanol (2) + <i>n</i> -octane (3)					
0.6972	0.1232	0.77552	1168	945	5
0.5944	0.2396	0.77805	1172	936	8
0.4864	0.3418	0.77812	1174	932	12
0.3850	0.4245	0.77680	1175	923	8
0.3378	0.4926	0.77950	1182	918	12
0.3059	0.4907	0.77602	1183	921	9
0.2294	0.6042	0.78090	1190	904	8
0.1329	0.6897	0.78050	1194	899	9
Methylethylketone (1) + 1-pentanol (2) + <i>n</i> -octane (3)					
0.7080	0.1114	0.77586	1152	971	35
0.5971	0.2365	0.77937	1164	947	30
0.4741	0.3081	0.77501	1176	933	17
0.4637	0.3510	0.77885	1182	919	15
0.3433	0.4733	0.78058	1192	902	14
0.3082	0.4773	0.77768	1186	914	22
0.2290	0.5959	0.78337	1199	888	19
0.1060	0.7143	0.78480	1210	870	16
0.0995	0.7493	0.78821	1211	865	21
Methylethylketone (1) + 1-hexanol (2) + <i>n</i> -octane (3)					
0.7055	0.1115	0.77596	1154	968	36
0.5991	0.2367	0.78046	1164	946	39
0.5243	0.2839	0.77843	1176	929	25
0.4735	0.3454	0.78080	1182	917	26
0.4196	0.3831	0.77989	1181	919	31
0.3365	0.4813	0.78340	1200	887	19
0.2247	0.6151	0.78825	1216	858	17
0.1026	0.7129	0.78753	1225	846	18
0.1112	0.7519	0.79311	1230	833	20

$$\rho = \frac{x_1 M_1 + x_2 M_2 + x_3 M_3}{V + V_{123}^E} \quad (2)$$

was used in these calculations. x_1, x_2, x_3 and M_1, M_2, M_3 denote the mole fractions and molecular weights of methylethylketone, 1-alkanol and *n*-octane respectively. V and V_{123}^E denote molar volume and excess volume respectively.

3. Results

The deviation in isentropic compressibility, ΔK_{s123} , for a ternary mixture is computed from the relation :

$$\Delta K_{s123} = K_{s123} - K_{s123}^{id} \quad (3)$$

where K_{s123} and K_{s123}^{id} are isentropic compressibilities of the real mixture and an ideal mixture respectively. The ideal isentropic compressibility is calculated using the relation

$$\Delta K_{s123} = \phi_1 K_{s,1} + \phi_2 K_{s,2} + \phi_3 K_{s,3} \quad (4)$$

where ϕ_1, ϕ_2, ϕ_3 and $K_{s,1}, K_{s,2}, K_{s,3}$ are volume fractions and isentropic compressibilities of methylethylketone, an alkanol and *n*-octane respectively. Isentropic compressibility of an ideal mixture is assumed to be additive in terms of volume fraction. Sound velocities and isentropic compressibilities of pure liquids are given in table 2. The experimental data for the mixtures are given in table 3.

The results in table 3 show that the deviation in isentropic compressibility is positive over the whole range of composition in the four ternary mixtures. The values of ΔK_{s123} for the four mixtures fall in the order:

$$1\text{-propanol} < 1\text{-butanol} < 1\text{-pentanol} < 1\text{-hexanol}.$$

The order suggests that increase in chain length of the alcohols contributes to an increase in the deviation of ΔK_{s123} .

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Explanation of symbols used

ρ	density, g cm ⁻³
u	sound velocity, ms ⁻¹
K	absolute temperature

$K_{s_{123}}$	isentropic compressibility of the real ternary mixture, TPa^{-1}
$K_{s_{123}}^{id}$	isentropic compressibility of an ideal ternary mixture, TPa^{-1}
$\Delta K_{s_{123}}$	deviation in isentropic compressibility of the ternary mixture, $(K_{s_{123}} - K_{s_{123}}^{id})$
V_{123}^E (exp)	experimental excess volume of ternary systems, $\text{cm}^3 \text{mol}^{-1}$
m_i	molecular weight of i th component in the ternary mixture
ϕ_i	volume fraction of i th component in the ternary mixture
x_i	mole fraction of i th component in the ternary mixture

Subscripts

1, 2, 3, components

Superscripts

E excess property

id ideal

Parentheses

exp experimental

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Synthesis, identification and analytical properties of the 5,5'-methylenedisalicylhydroxamic acid (MEDSHA)

L F CAPITÁN-VALLVEY*, F SALINAS and D GAZQUEZ

Department of Analytical Chemistry, Faculty of Sciences, University of Granada Granada, Spain

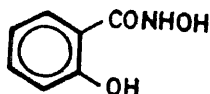
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Abstract. 5,5'-methylenedisalicylhydroxamic acid (MEDSHA) has been prepared by the reaction of diethyl-5,5'-methylenedisalicylate and hydroxylamine. The solubility, spectral and thermal characteristics, pK values, and reactions with metal ions are reported. Although MEDSHA itself gives precipitates with many metal ions, selectivity can be increased by appropriate control of pH and the use of masking agents, so that it can be used as a reagent for fewer cations.

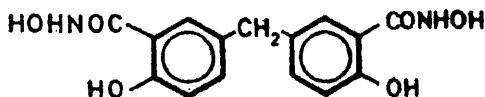
Keywords. Hydroxamic acid ; physicochemical properties ; analytical properties.

1. Introduction

In view of useful analytical applications of hydroxamic acids (Brandt 1960 ; Bass and Yoe 1966; Majumdar 1971) and of salicylhydroxamic acid (SHA, formula I) in particular (Bhaduri 1956; Majumdar and Mukherjee 1960; Pal and Chakraburty 1963 ; Poddar *et al* 1966), we synthesized and studied 5,5'-methylenedisalicylhydroxamic acid (MEDSHA, formula II) as a new analytical reagent. Since MEDSHA carries two SHA moities bridged through $-\text{CH}_2-$, we anticipated improved chelating abilities for it and enhanced insolubility characteristics of its metal derivatives. In this paper we report the synthesis, characteristics and analytical aspects of this reagent.



(I)



(II)

* To whom correspondence should be made.

All solvents and chemicals used were of the Reagent Grade.

Infrared spectra were recorded with a Beckman 4240 IR spectrophotometer in the $4000\text{--}250\text{ cm}^{-1}$ range, using the KBr pellet technique. The UV-VIS spectrophotometer used was a Beckman ACTA III (1-cm quartz cells). A Hewlett-Packard 5930 A mass spectrometer and a Hitachi Perkin-Elmer R-20 NMR were also used.

The simultaneous TG and DTA analyses of MEDSHA were performed with a Setaram GDTD-10 thermoanalyzer fitted with a B-70 electrobalance with thermocouples of Pt/Pt-Rh in alumina base. The measurements were made in static air atmosphere, at a heating rate of $2^\circ\text{ C min}^{-1}$. Approximately 10 mg samples were taken in an alumina crucible using calcinated α -alumina as reference material.

The solubilities of SHA and MEDSHA in several solvents, were measured by the method of Rose (1966) at $25 \pm 0.1^\circ\text{ C}$. The Metrohm E-536 potentiograph with glass and calomel electrodes was used for pH measurements. For determination of the dissociation constants of MEDSHA, both the potentiometric method described by Schwarzenbach *et al* (1947) and the spectrophotometric method described by Thamer (1955) were applied.

2.2. Synthesis of MEDSHA

5,5'-methylenedisalicylic acid (90 g), synthesized employing Oddo's method (Oddo 1940) was taken in ethanol (400 ml) and conc. H_2SO_4 (30 ml) was slowly added. After refluxing the reaction mixture for 3-4 hr, benzene (100 ml) was added. Water produced in the reaction was removed as an azeotrope ethanol-water-benzene (125 ml). The process was repeated five times and the reaction mixture was neutralized with NaHCO_3 to obtain a whitish crude ester. The product was extracted with benzene and recrystallized from ethanol. Yield 70% m.p. $100\text{--}103^\circ\text{ C}$. Elemental analysis, Found : C, 66.31 ; H, 5.80. Calculated : C, 66.28 ; H, 5.81 for $\text{C}_{19}\text{H}_{20}\text{O}_6$.

The ester (5 g) was slowly added to a stirred solution of hydroxylammonium-chloride (3.5 g) in 12% NaOH (50 ml). The reaction mixture was allowed to stand overnight and 2 N HCl was slowly added to precipitate MEDSHA. The product was purified by recrystallization from water and ethyl acetate-petroleum ether mixture to obtain a colourless powder (m.p. $170 \pm 1^\circ\text{ C}$) ; yield 90%, Elemental analysis, Found : C, 56.61 ; H, 4.63 ; N, 9.03. Calculated : C, 56.63 ; H, 4.40 ; N, 8.80 for $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_6$.

3. Results and discussion

3.1. Physicochemical properties of MEDSHA

3.1a. *Spectral and thermal characteristics.* The most important IR bands of MEDSHA are summarized in table 1. The stretching frequency observed at 1620 cm^{-1} and $2870\text{--}2955\text{ cm}^{-1}$ correspond to $\nu\text{C}=\text{O}$ and $\nu(\text{OH hydroxamic})$ respec-

tively. The low frequency of these bands indicates hydrogen bonding (Hadži and Prevorsek 1957; Mathis 1961; Roshama and Agrawal 1978).

On the other hand, it has been observed that the absorption band due to NH stretching vibration when free, appears around 3400 cm^{-1} , but strong hydrogen bonding in the solid state can cause lowering of this band (Mathis 1961). Similarly, the band at 3130 cm^{-1} is assigned to the stretching of the intramolecularly bonded OH phenolic group (Conley 1973).

Thus, it is concluded that the structural type III represents the most probable configuration of MEDSHA, in analogy with the proposed structure for SHA (Larsen 1978).

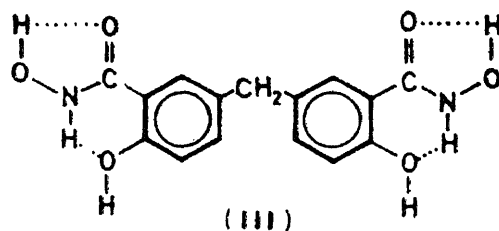


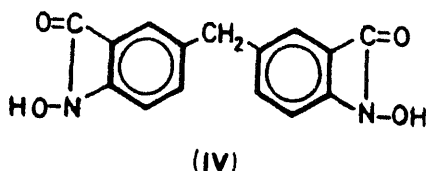
Table 1. Spectral properties of MEDSHA

IR	
νNH frequency, cm^{-1}	3290s*
$\nu\text{C}=\text{O}$ (amide I band) frequency, cm^{-1}	1620s
νOH hydroxamic frequency, cm^{-1}	2870s
	2918s
	2955s
νOH phenolic frequency, cm^{-1}	3130s, b
δNH (amide II band) frequency, cm^{-1}	1580s
$\nu\text{C}-\text{N}$ (amide III band) frequency, cm^{-1}	1420m
νNO frequency, cm^{-1}	970w
Mass s.	
	Relative Intensities (%)
M^+ ion (m/e 318)	1
base peak (m/e 33)	100
$[\text{M}-32]^+$	2
$[\text{M}-33]^+$	2
$[\text{M}-66]^+$	8
UV s.	
	ϵ ($1\text{ mol}^{-1}\text{cm}^{-1}$)
223 nm, λ_1 max (ethanol)	$2'95 \cdot 10^4$
310 nm, λ_2 max (ethanol)	$7'4 \cdot 10^2$
213 nm, λ_1 max (water)	$3'16 \cdot 10^4$
300 nm, λ_2 max (water)	$6'8 \cdot 10^2$

Mass spectral data of MEDSHA are listed in table 1. The ease with which MEDSHA decomposes at the melting temperature explains the very low abundance (1%) of the molecular ion in the spectrum of this compound. The base peak was located at m/e 33, the result of a loss of the NH_2OH groups from the molecular ion. Such a rearrangement agrees with the observed rearrangement of *o*-substituted aromatic amides (Simon and Clerc 1970).

The $[\text{M}-32]^+$ ion in the spectrum of MEDSHA indicates that oxygen is lost at the hydroxylamino positions (Bapat *et al* 1969 ; Akers *et al* 1975).

At the first stage of the thermal decomposition of MEDSHA, two molecules of water are eliminated, with a corresponding mass loss on the TG curve occurring between 150 and 202° C and an exothermic peak on the DTA curve at 172° C. The IR spectrum of a sample of MEDSHA heated at 170° C contains a strong absorption centered around 1750 cm^{-1} . This frequency is characteristic of stretching of a $\text{C}=\text{O}$ which belongs to a four-membered ring (Brewster *et al* 1970). These effects must be attributed to the N-hydroxylactam formation (IV).



Finally, the intermediate N-hydroxylactam decomposes in the temperature range 200–600° C, exhibiting a pronounced exothermic peak at 526° C.

The absorption maxima of MEDSHA and their molar extinction coefficients (ϵ), in aqueous and ethanolic solutions, are given in table 1. The absorption spectrum of MEDSHA shows a pH dependence in aqueous solution in the pH range of 6 to 12. This is shown by a hyperchromic and bathochromic effect of the maximum at 213 nm as the pH is increased. At the same time, the maximum at 300 nm is displaced bathochromically. In strong basic medium two new absorption maxima appeared at 325 nm and 243 nm. These effects are attributed to the dissociation steps.

3.1b. *Solubilities of SHA and MEDSHA in several solvents.* The results obtained (table 2) indicate that, in all instances, SHA is much more soluble than MEDSHA. However, we have found that the solubility of MEDSHA in water increases exponentially with temperature, according the equation $\ln S = 0.059 T - 4.047$ (S , g/l ; T , °C).

Spectrophotometric measurements indicate that the solutions of MEDSHA ($5 \cdot 10^{-5}$ M) in water are stable for at least five days, whereas the ethanolic solutions are stable for at least a month.

3.1c. *Acidity.* The data presented in table 3 show good agreement between the two sets of values. It seems reasonable to assume that both SHA and MEDSHA

Table 2. Solubilities of SHA and MEDSHA in several solvents at $25 \pm 0.1^\circ \text{C}$

Solvent	Solubility, g/l	
	SHA	MEDSHA
Water	2.93	0.08
Ethanol	60.18	30.05
Mothar oil	93.56	49.26
Acetone	54.06	10.72
Chloroform	1.91	0.88
Dioxane	67.42	8.20

Table 3. Acid dissociation constants of MEDSHA at $25 \pm 0.1^\circ \text{C}$ ($\mu = 0.1 \text{M}$, KClO_4)

	Method	
	Schwarzenbach	Thamer
pK_1	7.4 ± 0.1	7.5 ± 0.1
pK_2	8.3 ± 0.3	8.1 ± 0.1
pK_3	9.5 ± 0.1	9.9 ± 0.2
pK_4	10.9 ± 0.8	11.0 ± 0.6

(Kunitake *et al* 1976). There is some controversy regarding the assignment of pK_a values to the dissociations of the $-\text{OH}$, the $-\text{NH}$ and the $-\text{NOH}$ groups in SHA. While one of the investigating groups (Jabalpurwala *et al* 1964 ; Ingle and Khanolkar 1975 ; Bergmann and Tashma 1975) attributed the low pK_a value to the phenolic OH, this value is ascribed to the $-\text{CONHOH}$ function by another group (Exner and Kakač 1963 ; Dutt and Seshadri 1969 ; Desphande and Jahagirdar 1977). On the other hand, it is now an accepted fact that the hydroxamic acids belong to the N-acids (Bauer and Exner 1974).

In a recent study on metallic complexes of MEDSHA we have observed that the hydroxamic groups are more acidic than the phenolic ones (Gazquez 1981). Therefore, we feel that pK_1 and pK_2 of MEDSHA should be ascribed to the dissociation of the $-\text{NH}$ groups and pK_3 and pK_4 to the phenolic groups.

3.2. Chelating properties of MEDSHA

The reactions of 40 metal ions with MEDSHA were tested at different pH values, and the results are summarized in table 4.

Almost in all cases the respective complex compounds were precipitated, except those of Ag(I) and Au(III) . It has been observed that in Pd(II) , Mo(VI) , Fe(III)

Table 4. Reactions of MEDSHA with metallic ions. Effect of several masking agents on the metal-MEDSHA reaction.

Metal-MEDSHA reactions				Masking reactions							
Metal ion	Colour of complex	Optimum pH range	pD°	HCl 2N	H ₂ SO ₄ 2N	EDTA	F ⁻	tar	CN ⁻	SCN ⁻	PO ₄ ³⁻
Ag(I)	red	7-12	4'0			+ (>11) ^b			+ (>11)	+ (>11)	
Pb(II)	white	3-11	4'5			+ (5-7)			—		
Hg(I)	brown	3-9	4'2			+ (3-9)			+ (3-9)	+ (3-9)	
Hg(II)	yellow	5-9	3'4			+ (7-9)			+ (7-9)	+ (7-9)	
Bi(III)	white	0-12	4'6		—	+ (<3)					
Cu(II)	green	0-12	4'8	—	+	+ (0-12)		—	+ (3-12)	—	
Cd(II)	white	5-9	3'8			+ (5-7)			+ (5-7)		
Tl(III)	brown	3-7	3'6			+ (3-7)					
As ₂ (III)	red	0-12	3'9	+	+	+ (5-12)			+ (5-12)	+ (5-12)	
Pd(II)	yellow	0-12	4'7	+	+	+ (0-12)			+ (3-12)		
Sn(II)	white	0-5	5'0	—	—	—	p (0-5)	—			—
Sb(III)	white	0-4	4'6	p	—	—		+ (0-4)			
Mo(VI)	yellow	0-12	5'8	—	—	—					—
Os(VIII)	brown	0-5	4'0	+	+	+ (0-5)				+ (0-5)	
Al(III)	white	3-9	4'5			p (3-9)	+ (3-9)	—	—	—	+ (5-12)
Cr(III)	gray-green	5-12	5'0			+ (5-12)	—	—	—	—	—
Fe(III)	red	0-12	5'7	p	p	+ (0-7)	—	—	—	—	
Co(II)	brown	0-12	5'0	+	+	+ (>11)			+ (0-12)		
Co(III)	red-brown	0-12	5'0	+	+	+ (0-12)			+ (0-12)		

Zn(II)	white	5-9	4'0		+ (5-9)			p (5-9)	-	-	+
Mn(II)	white	5-7	4'0		+ (5-7)			-		-	p (
Be(II)	white	3-9	5'3		-			+ (5-7)			
V(V)	violet	0-7	5'8	-	-			-			
UO ₂ ²⁺	orange	3-11	5'0		+ (7-9)			-			+ (7-9)
Ti(IV)	yellow	0-9	6'0	-	-			+ (0-7)			
Zr(IV)	white	0-9	5'0	-	p (0-7)			p (0-7)			+
Th(IV)	white	0-9	5'2	+	+ (3-7)			p (0-7)			p (0-7)
In(III)	white	3-9	4'7		+ (3-7)			-			+
Y(III)	white	3-11	4'9		+ (3-7)			p (3-7)			
Sc(III)	white	0-11	5'2	+	+ (<3) + (3-5)			+ (<3)			p (
W(VI)	white	0-4	4'9	-	-			-			-
Ga(III)	white	0-7	4'6	p	p (<3)			-			-
La(III)	white	4-12	4'8		+ (4-7)			-			-
Co(IV)	red	3-12	5'0		+ (3-7)			p (3-7)			+ (3-7)
Ca(II)	white	5-11	5'2		+ (5-11)			p (5-11) + (5-11)			p (5-11)
Sr(II)	white	5-9	4'3		+ (7-9)			+ (7-9)			p (7-9)
Ba(II)	white	5-11	4'3		+ (5-7)			+ (5-7)			p (
Mg(II)	white	5-11	4'3		+ (5-11)			p (5-7)			+ (5-11)

tar = tartrate, $C_2O_4^{2-}$ = oxalate

(a) Detection limit (~1g mg metal/l)

(b) + indicates that the metal ion is masked completely ; Numbers in parentheses represent the pH range of masking

- indicates that reaction occurs with MEDSHA

p indicates that the metal ion is masked not completely

The solubilities of the complexes of MEDSHA are lower than those of the corresponding SHA complexes (Bhaduri 1956 ; Poddar *et al* 1966 ; Bhaduri and 1952 ; Chatterjee 1978), because of the higher molecular weight of MEDSHA. Moreover, this reagent possesses two chelation sites that could be utilized for chelating two metal ions simultaneously, giving rise thereby to very insoluble polynuclear complexes.

Although MEDSHA itself is a highly unselective reagent, selectivity can be increased by appropriate control of pH and the use of masking agents. Data on the influence of various masking agents on the reactions of metal ions with MEDSHA, in aqueous medium, are also summarized in table 4.

The strongest masking agent, over wide ranges of acidity, is EDTA. In the presence of EDTA only a few metals (Sn(II), Sb(III), Mo(VI), Be(II), V(V), Ti(IV) and Sc(III)) react completely with MEDSHA.

Cyanide is a very powerful masking agent for periodic groups IB and IIB, for Fe(II), Co(II), Co(III) and Ni(II), as they usually form extremely stable cyanide complexes.

On the other hand, it is obvious that strong acid medium increases the selectivity of MEDSHA with regard to some cations, such as Sn(II), Mo(VI), V(V), Ti(IV), Zr(IV) and W(VI). In fact, we have described a new simple method for the spectrophotometric determination of vanadium in HCl 2N medium (Salinas *et al* 1978). This method has been successfully used for determination of vanadium in petroleum crudes and derivatives and is free from the interference of nickel, iron (III) and several other elements which are often associated with vanadium.

The most characteristic reaction of the hydroxamic acids is the red-violet complexes which they form with iron(III) in acid medium. It is very interesting to note that iron(III) is precipitated by MEDSHA in the presence of F⁻, CN⁻ and PO₄³⁻.

As can be seen from table 4, V(V), Mo(VI), Ti(IV), W(VI) and Sn(II) form very stable complexes with MEDSHA. Only Ti(IV) is masked completely by F⁻ in the presence of MEDSHA. In view of these facts, we are investigating at present the use of a combination of two or more masking agents to improve the selectivity of new methods for the quantitative determination of these ions using 5-methylenedisalicylhydroxamic acid.

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Polarographic study of Eu(III)-hydroxamic acid complexes

P K BHANSALI and B I NEMADE*

Department of Chemistry, University of Bombay, Vidyanagari, Bombay 400 098, India

MS received 10 April 1982 ; revised 23 August 1982

Abstract. Complexes of europium(III) ion with two hydroxamic acids have been investigated by polarographic method of analysis at $30 \pm 0.1^\circ \text{C}$ and $\mu = 0.5 \text{ M}$ (KNO_3). In both hydroxamic acids phenylacetohydroxamic acid (PAHA) and acetohydroxamic acid (AHA), the electrode reaction was found to be quasireversible in nature, hence Gelling's method was used for evaluation of reversible half-wave potential and kinetic parameters. Formation of Eu(III)-hydroxamic acid complex was observed with metal ligand ratio 1 : 2 in aqueous solution.

Keywords. Phenylacetohydroxamic acid ; acetohydroxamic acid ; polarographic method ; quasireversible.

1. Introduction

In different non-complexing media (Vleck 1955, 1959 ; Gierst and Cornelissen 1960) the reduction of $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ is of irreversible to quasireversible nature. Literature survey revealed that there has been no study of the europium hydroxamic acid system by polarographic technique. Hence the present work has been undertaken.

2. Experimental

The current potential curves were recorded on a manual set-up using dropping mercury electrode (dme) and saturated calomel electrode (SCE) as reference electrode. The ionic strength was maintained at 0.5 with the help of potassium nitrate. Gelatin 0.002% was used as a maximum suppressor. All measurements were carried out at $30 \pm 0.1^\circ \text{C}$. The capillary had the following characteristics, $m = 1.94 \text{ mg/sec}$ and $t = 4.0 \text{ sec}$ in supporting electrolyte potassium nitrate in open circuit. The pH of the solution was measured with an expanded scale pH meter (Electronic Corporation of India Limited, Hyderabad, Model pH 821 B).

determined by pH titration technique of Irving and Rossotti (1954) were to be 9.20 and 9.40 respectively (Bhansali and Nemade 1982). Europium was prepared by dissolving europium oxide (Koch-light Lab. 99.9% pure) in perchloric acid and was standardised as described by Vogel.

3. Results and discussion

3.1. Europium-PAHA system

Well defined polarogram was obtained for Eu(III) in 0.5 M potassium nitrate half-wave potential at -0.670 V *versus* SCE which is in good agreement with reported values (Chandrasekaran 1970). Above pH = 5.2 formation of precipitate took place hence studies were restricted to a pH range of 4.0 to 5.0. With increase in hydroxamate ion concentrations the half-wave potentials shifted to more negative values indicating complexation. The half-wave potentials were determined from the plots of $\log i/i_d - i$ *versus* E (log-plots) and the slopes of these log-plots were of the order 60–90 mV. The reversible half-wave potential, kinetic parameters, *viz.*, α and K_s were evaluated by Gelling's method (Gelling 1962) (figure 1). The plot of $E'_{1/2}$ *versus* pA (data in table 1) resulted in a smooth curve which showed presence of more than one species whose slopes do not differ appreciably. The data were analysed by DeFord and Hume (DeFord and Hume 1951) method for evaluation of stability constants. The function $F_0(A)$ was calculated from shift in the half-wave potential obtained from the smooth curve of a plot of $E_{1/2}$ *vs* pA using method of DeFord and Hume (1951).

$$F_0(A) = \text{Antilog} \left[0.4343 \frac{nF}{RT} (E_{1/2(s)} - E_{1/2(c)}) + \log \frac{I_{(s)}}{I_{(c)}} \right]$$

$$= 1 + \beta_1 [A] + \beta_2 [A]^2 + \beta_3 [A]^3 + \dots + \beta_n [A]^n$$

where, $E_{1/2(s)}$ and $E_{1/2(c)}$ refer to the half-wave potential of the uncomplexed and complexed ions respectively and $I_{(s)}$ and $I_{(c)}$ are the corresponding diffusion currents. β 's refer to the overall stability constants, and $[A]$ is the concentration of the ligand. Values of F_i functions obtained at different ligand concentrations $[A]$ are given in table 1. The values of the stability constants obtained are

$$\beta_1 = 2.0 \times 10^7 \quad \text{and} \quad \beta_2 = 2.7 \times 10^{14}$$

3.2. Europium-AHA system

In the case of AHA the formation of precipitate was observed at pH > 5.8. Hence studies were therefore made at pH below 5.8. The slopes of the log-plots

Table 1. Europium-PAHA system. Effect of ligand concentration on half-wave potential and values of F_j functions.

$[\text{Eu}^{3+}] = 0.6 \text{ mM}$, $\mu = 0.5 \text{ M KNO}_3$; Temp. = 30°C

$m^2/a \cdot t^{1/6} = 1.96 \text{ mg}^{2/3} \cdot \text{sec}^{-1/6}$; $\text{pK} = 9.20$

$[\text{HA}] \times 10^3$ M	$[\text{A}] \times 10^7$ M	pH	pA	$E_{1/2}$ —V vs.	$E'_{1/2}$ SCE	α	i_d μA	$-\log K_s$	$F_0(\text{A}) \times 10^{-1}$ Exptl.	$F_1(\text{A}) \times 10^{-8}$	$F_2(\text{A}) \times 10^{-8}$	$F_0(\text{A}) \times 10^{-12}$ Calcd.
0	...	...	...	0.670	0.648	0.27	1.88	3.026	...	...	...	...
2.0	0.6607	4.72	7.18	0.684	0.677	0.16	1.82	2.968	0.3519	0.3813	2.744	0.3500
2.0	0.7586	4.77	7.12	0.690	0.684	0.29	1.81	3.028	0.3969	0.3915	2.524	0.4071
2.0	0.7943	4.80	7.10	0.696	0.687	0.14	1.80	2.908	0.4148	0.3963	2.471	0.4252
8.0	1.349	4.43	6.87	0.701	0.691	0.29	1.78	2.888	0.7171	0.4575	1.909	0.8611
24.0	2.089	4.14	6.68	0.717	0.710	0.19	1.76	2.988	1.560	0.6989	2.388	1.696
8.0	2.630	4.72	6.58	0.746	0.732	0.14	1.69	3.228	2.778	1.018	3.109	2.494
4.0	2.884	5.06	6.54	0.748	0.737	0.24	1.68	3.058	3.258	1.095	3.103	2.923
32.0	3.311	4.29	6.40	0.758	0.749	0.26	1.62	3.205	5.525	1.363	2.921	3.722
12.0	3.981	4.82	6.30	0.775	0.770	0.22	1.63	3.088	12.350	2.444	...	...

Table 2. Europium-ANA system. Effect of ligand concentration on half wave potential and values of F_1 functions,

$[\text{Eu}^{3+}] = 0.6 \text{ mM}$; $\mu = 0.5 \text{ M KNO}_3$; Temp. = 30°C

$m^{2/3} \cdot t^{1/6} = 1.96 \text{ mg}^{2/3} \cdot \text{sec}^{-1/2}$; $pK = 9.40$

$[\text{HA}] \times 10^3$ M	$[\text{A}] \times 10^6$ M	pH	pA	E_1/E_2 vs.	$E_{1/2}$ SCE	a	i_d μA	$-\log K_s$	$F_0(\text{A})$ Exptl.	$F_1(\text{A}) \times 10^6$	$F_2(\text{A}) \times 10^{11}$	$F_0(\text{A})$ Calcd.
0	...	...	...	0.670	0.648	0.27	1.88	3.028	...	...	...	...
16.0	1.738	5.44	5.76	0.677	0.663	0.22	1.83	3.018	1.825	0.4447	1.523	1.796
24.0	2.754	5.46	5.56	0.682	0.674	0.18	1.80	3.008	2.828	0.6636	1.756	2.709
32.0	3.548	5.44	5.45	0.698	0.688	0.18	1.76	2.978	3.782	0.7839	1.702	3.653
40.0	4.786	5.48	5.32	0.700	0.690	0.19	1.77	3.028	5.731	0.9884	1.689	5.526
56.0	6.457	5.46	5.19	0.711	0.700	0.21	1.73	3.038	8.936	1.229	1.625	8.833
40.0	7.079	5.65	5.15	0.715	0.705	0.21	1.71	2.998	9.760	1.237	1.493	10.292
48.0	7.413	5.52	5.13	0.722	0.708	0.16	1.68	3.038	11.144	1.368	1.603	11.127
56.0	8.913	5.60	5.05	0.730	0.716	0.26	1.66	3.058	15.324	1.607	1.601	14.369
56.0	10.720	5.68	4.97	0.741	0.723	0.21	1.62	3.214	20.531	1.872	1.532	21.317

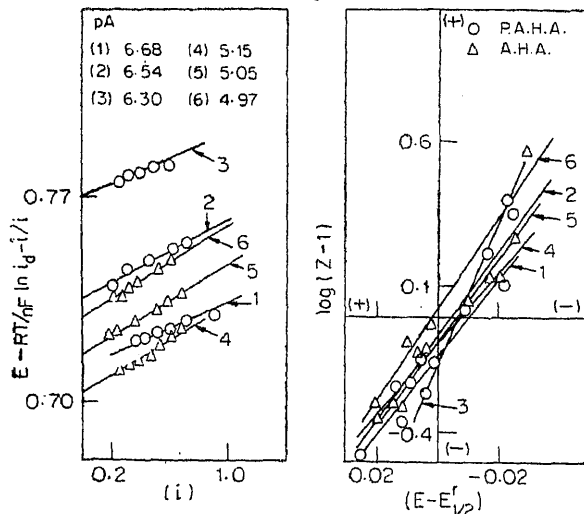


Figure 1.

found in the range 60–87 mV. The reversible half-wave potentials and kinetic parameters were evaluated using Gelling's method (figure 1 and table 2). Two complexes were identified with stability,

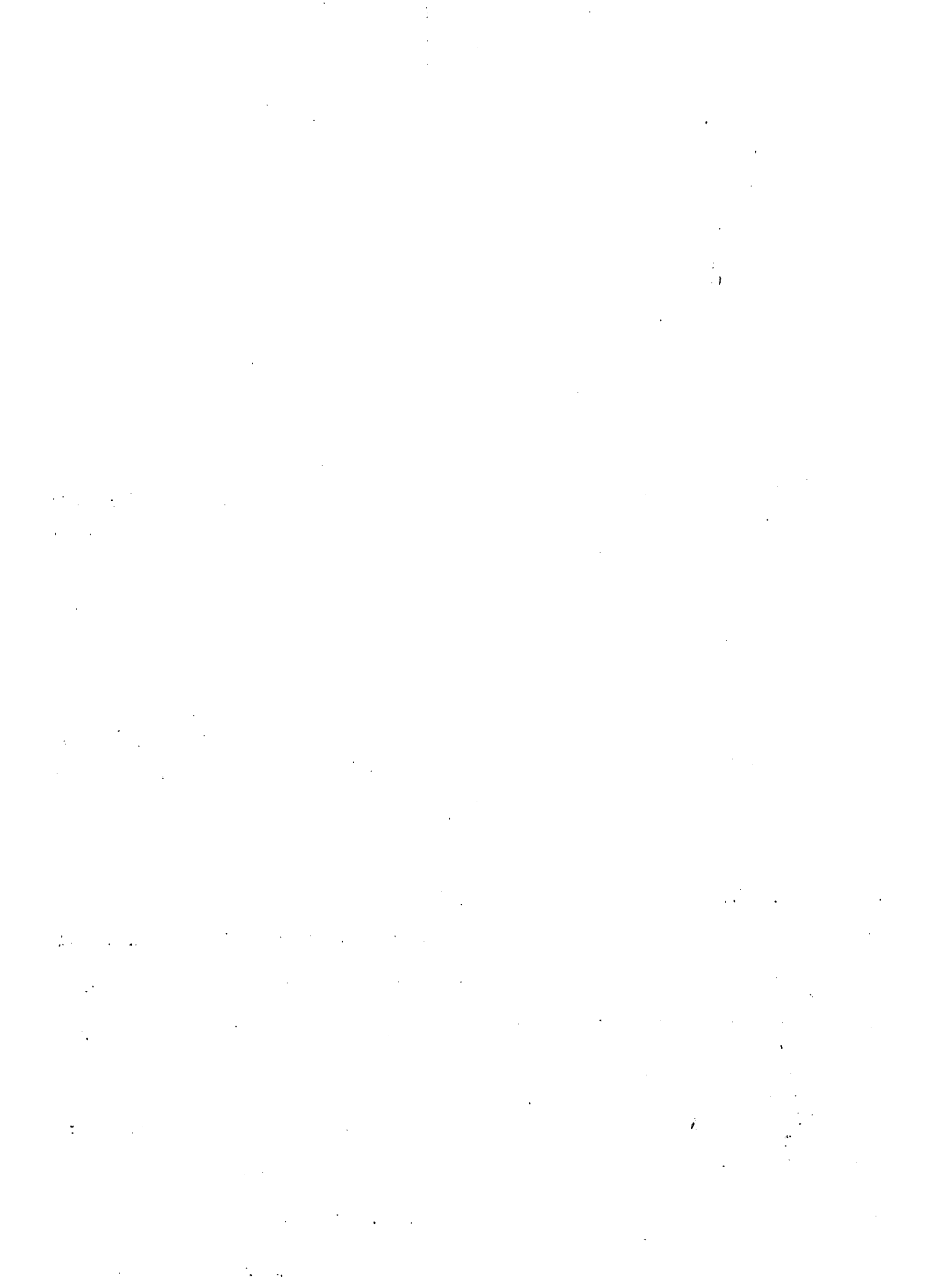
$$\beta_1 = 1.8 \times 10^5 \text{ and } \beta_2 = 1.6 \times 10^{11}.$$

Results showed that complexes formed by PAHA are stronger than those of

AHA the hydroxamic acid functional groups $\begin{array}{c} \text{O} \quad \text{H} \\ \parallel \quad | \\ -\text{C}-\text{N}-\text{OH} \end{array}$ acts as bidentate ligand, and chelation usually occurs (Agrawal 1977), by the substitution of hydrogen atom of hydroxylamine by metal atom and ring closure by carbonyl oxygen atom.

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Redox reactions in non-aqueous media: determination of hydrazine and its organic derivatives with lead(IV) acetate

BALBIR CHAND VERMA, SAROJ CHAUHAN, JAGMOHAN BUTAIL and RAJNISH KUMAR SOOD

Department of Chemistry, Himachal Pradesh University, Simla 171 005, India

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Abstract. Lead(IV) acetate (in glacial acetic acid) has been described as an oxidimetric reagent for the determination of hydrazine and its organic derivatives in glacial acetic acid medium. The end-points have been detected visually using quinalizarin as an indicator and potentiometrically using platinum wire indicator electrode and modified-calomel reference electrode. The method is simple, accurate, reliable and widely applicable.

Keywords. Lead(IV) acetate ; hydrazine ; non-aqueous titration ; quinalizarin.

1. Introduction

The usefulness of non-aqueous redox methods for the determination of compounds which are insoluble in water, or react with water to undergo hydrolysis/oxidation or are decomposed by the media, *i.e.*, acids, bases, etc. of aqueous redox titrations, is well established. Hydrazine is a powerful reducing agent and majority of the analysis of hydrazine or its organic derivatives is based on this behaviour of hydrazino group. Although this group is readily oxidised, yet its oxidation in aqueous media is affected only under properly controlled conditions ; the nature and proportion of the oxidation products depend upon the nature of the oxidants and experimental conditions, *i.e.*, concentration of reactants, temperature, pH, etc. The oxidation of hydrazines in acidic medium even with moderate oxidising agents is slow, and in alkaline medium the compounds are quite susceptible to air oxidation. Many organic derivatives of hydrazine, especially those containing aryl groups are only sparingly soluble in water. The application of non-aqueous redox methods to the determination of hydrazine and its organic derivatives is of great interest and scope. Only limited efforts have been made to apply such methods to the analysis of these compounds.

The present communication reports the use of lead(IV) acetate (in glacial acetic acid) for the visual and potentiometric determination of hydrazine and its organic derivatives in glacial acetic acid medium. Quinalizarin has been found

to be a suitable indicator in visual titrations. The end-point is marked by a sharp colour change from red to blue except in cases of *p*-nitrophenylhydrazine and 2,4-dinitrophenylhydrazine where it is from red to bluish green. The potentiometric titrations were performed using platinum wire indicator electrode and a modified-calomel reference electrode. A sharp jump in potential was observed at the equivalence point in each titration.

2. Experimental

2.1. Apparatus

Potentiometric titrations were performed with a Toshniwal CLO6A potentiometer using bright platinum wire indicator electrode and modified-calomel (saturated methanolic potassium chloride solution instead of aqueous) reference electrode. The solutions were magnetically stirred during the titrations.

2.2. Standard lead(IV) acetate solution

Standard lead(IV) acetate, 0.05 N in glacial acetic acid was prepared by reacting Pb_3O_4 in glacial acetic acid (Berka *et al* 1960) and standardized iodometrically (Berka *et al* 1965).

2.3. Hydrazines

Carboxylic acid phenylhydrazides were prepared and purified by the method of Stempel and Schaffel (1942). Phenylhydrazine was distilled before use. *p*-nitrophenylhydrazine and 2,4-dinitrophenylhydrazine were recrystallised before use. Hydrazine hydrate was used as received.

2.4. Indicator solution

Quinalizarin (1,2,5,8-tetrahydroxy anthraquinone) indicator was used as 0.2% solution in glacial acetic acid.

2.5. Solvent

Glacial acetic acid (BDH, AR) was used as received.

2.6. Procedure

Aliquots (1–5 ml) of solution in glacial acetic acid of each hydrazine were taken in titration vessels. For visual titrations 20–30 ml of glacial acetic acid and 5–10 drops of quinalizarin indicator were also added. Each solution was titrated at room temperature (25°C) with standard (0.05 N) lead(IV) acetate to a colour

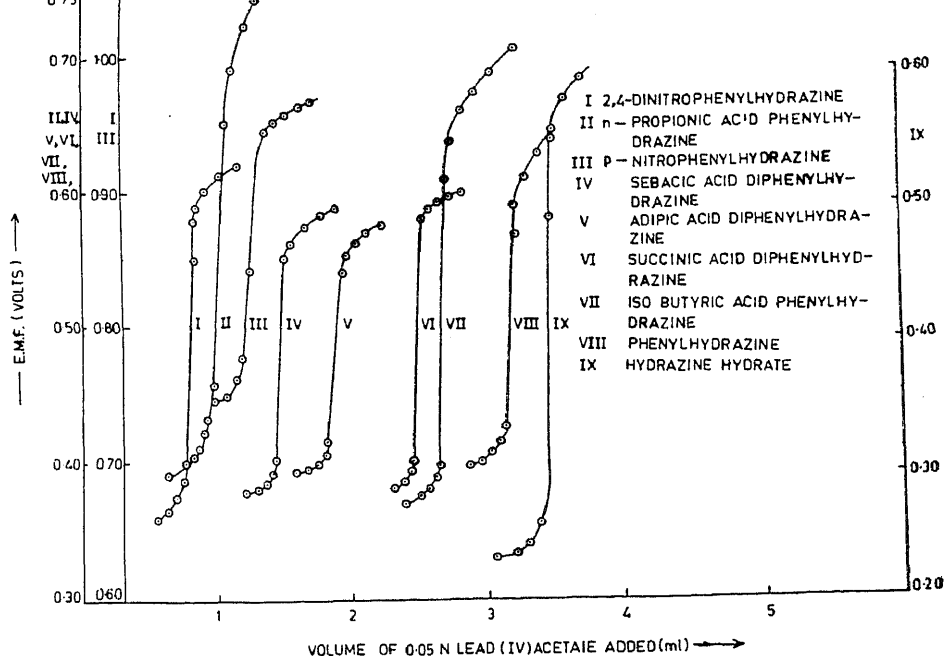


Figure 1.

platinum-modified calomel electrode assembly. A series of potentiometric titrations were performed with different amounts of each compound. Potentiometric titrations, one for each hydrazine, are represented by curves I to IX in figure 1.

From the volume of oxidant solution used corresponding to the end-points in visual and potentiometric titrations, the amount of each hydrazine was calculated. The results are given in table 1.

3. Results and discussion

The usefulness of lead(IV) acetate (in glacial acetic acid) in oxidimetry is well established. The oxidant had been used for the determination of a number of reducible compounds including some hydrazines (Ashworth 1964), but the analysis has been carried out in aqueous acidic media and that obviates one of the advantages of non-aqueous oxidimetry, with lead(IV) acetate.

In the present work, the oxidant has been found to oxidise hydrazines smoothly in glacial acetic acid, permitting the use of quinalizarin indicator in visual titrations. Fluctuations in potentials were observed when saturated (aqueous) calomel electrode was used as reference electrode. When the titrations were, however, performed with a modified-calomel reference electrode, the potentials stabilized rapidly. That modified calomel is a suitable electrode for non-aqueous

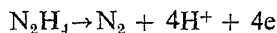
Table 1. Determination of hydrazine and its organic derivatives with lead(IV) acetate.

Hydrazines	Values are mean of ten determinations with standard deviation ($\pm$)			
	Amount found*, mg		Amount found**, mg	
	Visual method	Potentiometric method	Visual method	Potentiometric method
Hydrazine hydrate	4.03, 0.088	4.01, 0.050	12.11, 0.082	12.08, 0.078
<i>n</i> -Propionic acid phenylhydrazide	4.04, 0.060	3.98, 0.058	11.91, 0.101	11.96, 0.083
<i>Iso</i> -butyric acid phenylhydrazide	3.96, 0.071	3.98, 0.065	11.90, 0.093	11.96, 0.059
Succinic acid diphenylhydrazide	4.00, 0.081	4.00, 0.077	11.90, 0.078	11.95, 0.072
Adipic acid diphenylhydrazide	3.97, 0.091	3.98, 0.072	12.09, 0.100	12.07, 0.088
Sebacic acid diphenylhydrazide	4.02, 0.091	4.02, 0.083	12.06, 0.088	12.05, 0.073
Phenylhydrazine		3.96, 0.092		12.11, 0.088
<i>p</i> -Nitrophenylhydrazine	3.95, 0.076	3.97, 0.075	11.96, 0.096	12.04, 0.088
2,4-dinitro-phenylhydrazine	3.96, 0.086	3.98, 0.081	12.08, 0.100	11.94, 0.078

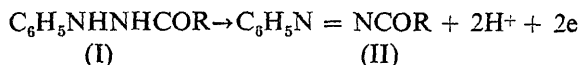
* Amount taken, 4 mg ; ** Amount taken, 12 mg.

in redox titrations in acetic acid medium using platinum-saturated (water) calomel electrode assembly have been described by many workers (Kratochvil 1966).

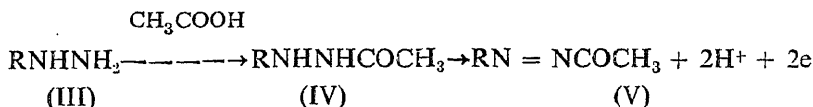
The results (table 1) indicate that whereas hydrazine is oxidised with a four-electron change, monosubstituted hydrazides (I)



(*n*-propionic acid and *iso*-butyric acid phenylhydrazides as well as adipic acid-, succinic acid- and sebacic acid diphenylhydrazides) are oxidised with a two electron change per hydrazino group with the oxidant. That phenylhydrazides (I) could be oxidatively converted



and 2,4-dinitrophenylhydrazines) also with a two-electron change. The course of reaction may be described as :



Phenylhydrazines (III) are first converted to hydrazides (IV) with the solvent before they are oxidised to the corresponding diazonium compounds (V) in the same manner as described for monosubstituted hydrazides earlier. This role of the solvent that it reacts with monosubstituted hydrazines to form the corresponding hydrazides is also known (Streuli and Averell 1970).

4. Conclusion

The proposed methods for the determination of hydrazine and its organic derivatives with lead(IV) acetate in glacial acetic acid medium are simple, accurate, reliable and of wide applicability. Since a solution of lead(IV) acetate prepared by the reaction of Pb_3O_4 with glacial acetic acid if stored in closed flask is highly stable even at dilutions (Zyka and Berka 1962), the method can be extended to the microdetermination of hydrazines.

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Kinetics of chlorination of ketones by 1-chlorobenzotriazole

P S JAYARAMAN, S SUNDARAM and
N VENKATASUBRAMANIAN*

Department of Chemistry, Ramakrishna Mission, Vivekananda College, Mylapore,
Madras 600 004, India

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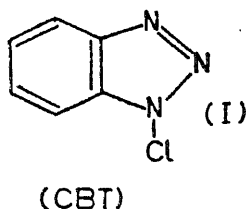
Abstract. The kinetics of chlorination of aliphatic, aralkyl and alicyclic ketones by 1-chlorobenzotriazole (CBT) have been studied in aqueous acetic acid media. In the presence of a mineral acid (HClO_4), the order of the reaction with respect to [ketone] is one and that with respect to [CBT] is zero, suggesting the enolisation of ketone as the slow step, followed by a fast attack of the halogenating species. A primary kinetic isotope effect ($k_H/k_D = 6.6$) is also noticed, when acetone and acetone- d_6 are used as the substrates. Initial addition of chloride ion leads to a first order dependence on [CBT] and a fractional order (0.6) on [acetone]. Thermodynamic parameters for the reaction have also been reported. A negative Hammett reaction constant ($\rho = -0.57$) has been obtained for the halogenation of substituted acetophenones by CBT.

Keywords. 1-Chlorobenzotriazole; chlorination; aliphatic, aralkyl and alicyclic ketones; primary isotope effect; acid catalysis; Hammett reaction constant.

1. Introduction

The halogenation of carbonyl compounds especially the enolisable ones has been the subject of many investigations and the kinetic and synthetic aspects are well documented (de la Mare 1976; Bell 1973). Among the various halogenic electrophiles, molecular halogens have been the most exploited. It has been well established that in acidic media at sufficiently high concentration of halogen, the rate is dependent only on the enolisation of ketone, though there have been instances (Bell and Page 1973; Toullec and Dubois 1973; Bell and Yates 1962) where the generation of a halogenating species turns out to be rate-determining. The prior formation of an adduct (Marshall and Roberts 1971) catalysis by ammonium ions (Bender and Williams 1966) and competing reactions leading to rearrangement (Warnhoff and Teo 1973) are also known to result in complicated kinetic situations. An interesting observation of the rate of chlorination being independent of [ketone] has been reported (Balasubramanian and Thiagarajan 1976) in which the sodium salt of N-chloro toluene-*p*-sulphonamide (Chloramine-T) functions as the halogen source. A study of the halogenation of phenols by the recently developed reagent (Rees and Storr 1968), 1-chlorobenzotriazole

(CBT) (I) has yielded many interesting results (Srinivasan 1977) and the work we report here comprises of an extension of our kinetic and mechanistic studies with CBT to typical carbonyl systems.



2. Experimental

1-Chlorobenzotriazole was prepared by the method of Rees and Storr from benzotriazole (E Merck sample, melting point 96°C). It was dried and recrystallised (melting point $105\text{--}106^{\circ}\text{C}$) from *n*-hexane.

The liquid organic compounds were purified by distillation from an all-glass apparatus. The solid organic compounds were of extra pure variety. All the inorganic chemicals used were of AR grade. Analar grade acetic acid (BDH) was used after purification by the usual procedure. (Orton and Bradfield 1927).

Solutions of ketone were prepared in aqueous acetic acid mixtures. CBT was dissolved in 100% acetic acid. Both ketone and CBT solutions were thermostated for two hours before each run and they were mixed. 5 ml aliquots of the reaction mixture were pipetted out at regular intervals and quenched in 10 ml of 5% KI solution. 20 ml of 1N H_2SO_4 was added and the liberated iodine was titrated against standard sodium thiosulphate to a starch end point (Berka *et al* 1965).

The reactions were carried under pseudo-molecular conditions. The first order rate constants were evaluated by the numerical method from the integrated rate expression. The zero order rate coefficients were evaluated from a plot of [CBT] against time, the positive slope giving the rate constant. The rate constants were reproducible within $\pm 5\%$. The kinetics were followed nearly to 3 half-lives and reactions were found to be smooth.

3. Product analysis

11.0 g of acetophenone was treated with 1.32 g of CBT in presence of 0.1M HClO_4 and in 50% HOAc–50% H_2O (v/v) medium. When the reaction was complete, acetic acid was neutralised by the addition of solid sodium bicarbonate. The crude crystalline mixture was extracted with chloroform (5×25 ml). It was shaken with dilute hydrochloric acid to remove 1-H benzotriazole. Chloroform was removed by evaporation and the crude compound was recrystallised from alcohol. The product ω -chloroacetophenone has been identified by TLC and by mixed melting point method (m.p. 55°C).

4. Results and discussion

4.1 Chlorination in aqueous acid medium

found to be zero order in [CBT] (as evidenced by the linearity of a plot of $\{[\text{CBT}]_0 - [\text{CBT}]_t\}$ vs time as also by the constancy of values obtained by the substitution of data in the corresponding rate expression), while it is dependent on the first power of the concentration of ketone (table 1). The order with respect to ketone has been derived from a linear plot of $\log k_0$ vs [ketone], the slope of which is found to be unity.

The reaction is sluggish in the absence of acids. Perchloric and sulphuric acids produce approximately the same catalytic effect, the order with respect to acid in both cases being unity (table 2). The rate law, therefore, is

$$\text{Rate} = k_2 [\text{ketone}] [\text{acid}] \quad (1)$$

Table 1. Effect of concentration of reactants.

[substrate] 10^3 M	[CBT] 10^3 M	$k_0 \times 10^7$ $\text{mol l}^{-1}\text{s}^{-1}$	$k'_1 \times 10^6$ s^{-1}
(a) <i>Acetone</i>			
3.18	4.53	6.51	...
3.18	3.81	6.42	...
3.18	3.20	6.34	1.99
1.91	3.20	3.77	1.97
2.55	3.20	5.07	1.99
5.47	3.20	11.3	2.06
6.88	3.20	14.2	2.06
8.25	3.20	17.6	2.13
9.63	3.20	20.0	2.07
(b) <i>Acetophenone</i>			
5.37	5.39	5.34	...
5.37	2.64	5.19	...
5.37	1.62	4.24	0.79
3.42	1.62	2.60	0.76
2.15	1.62	1.68	0.78
1.79	1.62	1.32	0.74
1.23	1.62	0.91	0.73
(c) <i>Cyclopentanone</i>			
3.47	4.51	16.9	...
3.47	3.96	16.2	...
3.47	3.01	16.6	4.80
4.16	3.01	20.4	4.90
5.20	3.01	25.2	4.85

Table 2. Effect of hydrogen ion concentration

[H ⁺] M	10 ⁷ k ₀ mol l ⁻¹ s ⁻¹		10 ⁶ k ₁ ' s ⁻¹	
	HClO ₄ *	H ₂ SO ₄ **	HClO ₄ *	H ₂ SO ₄ **
(a) Acetone				
0.05	2.74	3.67	5.48	7.33
0.10	5.56	7.29	5.56	7.29
0.15	8.04	10.8	5.36	7.20
0.20	10.55	14.5	5.28	7.25
0.24	12.5	...	5.20	...
* [CBT] : 2.37 × 10 ⁻³ M [A] : 2.57 × 10 ⁻² M				
** [CBT] : 3.22 × 10 ⁻³ M [A] : 3.34 × 10 ⁻² M				
(b) Acetophenone				
0.05	1.35	1.56	2.70	3.12
0.10	2.64	3.09	2.64	3.09
0.20	4.77	6.03	2.40	3.02
0.30	...	9.33	...	3.11
0.40	10.4	...	2.51	...
* [CBT] : 2.93 × 10 ⁻³ M [B] : 3.03 × 10 ⁻² M				
** [CBT] : 3.22 × 10 ⁻³ M [B] : 3.22 × 10 ⁻² M				
(c) Cyclopentanone :				
0.10	16.6	...	16.4	...
0.15	24.0	...	16.0	...
0.20	34.4	...	17.2	...
* [CBT] : 3.04 × 10 ⁻³ M [C] : 3.47 × 10 ⁻² M				

Solvent : 50% HOAc-50% H₂O (v/v) Temp. : 40° C
 $k_1 = k_0/[\text{acid}]$

Table 3. Catalysis by acids on acetone system.

[H ⁺] M	Time in min for 50% reaction		
	HClO ₄	H ₂ SO ₄	HCl
0.05	65	70	34
0.10	35	40	19

However, all other conditions remaining the same, for a given concentration, hydrochloric acid accelerates the reaction more than sulphuric or perchloric acids (table 3). This is traceable to a cumulative catalysis by H^+ and Cl^- . Such accelerations by HCl have been reported in the chlorination of phenols (Balasubramanian and Thiagarajan 1975) and oxidation of secondary alcohols by chloramine-T (Natarajan and Thiagarajan 1975) and N-chlorosuccinimide (Srinivasan and Venkatasubramanian 1973).

4.2 Effect of added salts

The addition of a neutral salt such as sodiumperchlorate does not produce any appreciable change in rate. But the addition of sodium chloride in presence of a mineral acid, not only enhances the rate but brings about a change in the rate picture itself. This is discussed in a later section. However, the effect of initially added chloride, in the absence of any mineral acids is not as much as it is in the presence of acid (tables 4 and 11). For example at $[NaCl] = 0.053\text{ M}$,

Table 4. Effect of added sodium chloride in the absence of mineral acid.

$[NaCl] \text{ } 10^2 \text{ M}$	$10^5 k_1 \text{ s}^{-1}$
Nil	very slow
2.2	7.83
5.3	12.2
8.8	16.8
5.3	75.3*

* in presence of 0.1 M HClO_4

Temp.: 40°C

Solvent: $50\% \text{ HOAc}-50\% \text{ H}_2\text{O}$ (v/v)

$[\text{Acetone}] : 3.28 \times 10^{-2} \text{ M}$

$[\text{CBT}] : 3.26 \times 10^{-3} \text{ M}$

k_1 is the rate constant for the first order loss of CBT in presence of initially added Cl^- .

Table 5. Kinetic isotope effect.

$[\text{substrate}] \text{ } 10^2 \text{ M}$	$10^8 k_0$ $\text{mol l}^{-1} \text{ s}^{-1}$	$10^6 k'_1$ s^{-1}	$k'_{1(\text{H})}/k'_{1(\text{D})}$
Acetone			
2.55	50.7	19.9	6.6
3.18	63.4	19.9	
Acetone- d_6			
2.56	7.48	2.90	3
3.19	9.58	2.97	

Solvent: $50\% \text{ HOAc}-50\% \text{ H}_2\text{O}$ (v/v)

Temp.: 40°C

the rate constants for the first order loss of CBT in the absence and in the presence of perchloric acid are $1.22 \times 10^{-4} \text{ s}^{-1}$ and $7.53 \times 10^{-4} \text{ s}^{-1}$ respectively.

4.3 Kinetic isotopic effect

The chlorination of acetone- d_6 by CBT is a smooth reaction. The order with respect to the substrate was obtained by varying its initial concentration, as also by a plot of $\log k_0$ vs $\log [\text{substrate}]$, whose slope is unity. The chlorination of acetone- d_6 proceeds about 6.6 times slower than that of acetone itself (table 5) such a reasonable value (Reitz and Kopp 1939) for the primary kinetic isotope effect is indicative of a rate-determining enolisation step (Reitz 1937).

Table 6. Effect of solvent composition on rate.

HOAc-H ₂ O % (v/v)	$10^7 k_0 \text{ mol l}^{-1} \text{ s}^{-1}$		
	(a)	(b)	(c)
40-60	6.74	2.22	5.90
50-50	7.00	2.48	6.71
60-40	10.4	2.97	7.43
70-30	13.7	3.74	...
80-20	...	5.15	...

[HClO₄] : 0.1 M [CBT] : $3.17 \times 10^{-3} \text{ M}$ Temp. : 40° C
 (a) [acetone] : $3.27 \times 10^{-2} \text{ M}$ (b) [Acetophenone] : $3.20 \times 10^{-2} \text{ M}$
 (c) [Isobutylmethylketone] : $3.31 \times 10^{-2} \text{ M}$

Table 7. Effect of Structural variations.

Substrate	$10^5 k'_1 \text{ s}^{-1}$
Acetone	1.99
Acetone- d_6	0.30
Ethylmethylketone	2.54
Isobutylmethyl ketone	2.03
3,3, dimethyl but-2-one	1.14
Acetophenone	0.76
Propiophenone	0.33
Cyclopentanone	4.73
Cyclohexanone	12.9
Cycloheptanone	2.51
Cyclooctanone	21.1

Solvent : 50% HOAc-50% H₂O (v/v) Temp. : 40° C

The rate of chlorination of ketones is dependent on the composition of the solvent medium used. Thus, in aqueous acidic media, increasing volume percentages of acetic acid increases the rate (table 6).

4.5 Effect of variations in the structure of the substrate

A wide range of variation in the substrate moiety has been employed to investigate the importance of structural effects in these reactions. A representative selection of aliphatic, aralkyl and alicyclic ketones has been used and the rate data presented (table 7). The results of the acetophenone-CBT reaction have been cast into a Hammett plot of $\log k_1'$ vs σ and the reaction constant ρ at 40° C is found to be -0.57 (table 8).

4.6 Effect of added benzotriazole

In the halogenation of phenols, anilides and toluenes by CBT (Srinivasan 1977), benzotriazole (BTH) which is one of the products of the reaction, when initially added produced a marked rate retardation accompanied by a change in the rate picture itself. Similar effects have also been reported in the oxidation of benzylalcohols by CBT (Rangadurai 1978). In the present investigation, however, initial addition of BTH produced only a small retardation and this is not attended by any change in the order on [CBT] or [Ketone]. Also, initial addition of BTH, brings about only a small retardation in rate even when the reaction is carried out in presence of chloride ions (table 9).

4.7 Activation parameters

The kinetics have been investigated in the temperature range 30° to 50° C. The rate constants and the activation parameters (as evaluated from plots of $\log k_1'$ vs T^{-1}) are presented in table 10. The isokinetic relationship has been tested for in the light of Exner's statistical treatment (Exner 1964, 1970). A plot of $\log k_{45^\circ}$ vs $\log k_{30^\circ}$ is linear indicating the operation of this relationship. The value of the isokinetic temperature calculated from the slope of the line is 64.6° K. The linear relationship (Bowden *et al* 1964) in the Exner plot is suggestive of a unified mechanism for all the compounds. Since the isokinetic temperature is well below the reaction temperature, the application of Hammett's equation is justified and with increase in temperature, the reaction constant may be expected to increase. Indeed such an increase is observed for the chlorination of acetophenones ($\rho = -0.53, -0.57$ and -0.63 at 30°, 40° and 50° C respectively). A plot of $\Delta H^\ddagger$ vs $\Delta S^\ddagger$ is also linear giving a value of 285° K for the isokinetic temperature, which is near the experimental temperature and this could arise out of an error slope. It may be pointed out that this value is markedly different from the one obtained by Exner's method. This only emphasises the caution that must be exercised in making such plots between two mutually depen-

Table 8. Evaluation of the reaction constants for substituted Acetophenones.

X-	σ	$10^6 k'_1 \text{ s}^{-1}$
H	O	7.60
<i>p</i> -NO ₂	+0.78	3.28
<i>m</i> -NO ₂	+0.71	2.70
<i>p</i> -CH ₃	-0.17	10.8
<i>p</i> -Cl	+0.23	6.35
<i>m</i> -Cl	+0.37	4.38
<i>p</i> -COCH ₃	+0.50	5.06

Solvent: 50% HOAc-50% H₂O (v/v) Temp.: 40° C

[HClO₄]: 0.1 M [X-C₆H₄-COCH₃]: 3.26×10^{-2} M [CBT]: 3.17×10^{-3} M

σ values are taken from J Hine, *Physical organic chemistry*, McGraw-Hill Book Co.,

New York, 1962, p. 87

Correlation coefficient: 0.975; $\rho = -0.57$ $k'_1 = k_0/[\text{ketone}]$

Table 9. Effect of added Benzotriazole.

BTH) 10 ³ M		10 ⁷ K ₀ mol l ⁻¹ s ⁻¹		
		*Acetone	**Ethylmethyl ketone	***Acetophenone
(a)	Nil	7.00	8.23	2.48
	1.82	...	6.83	2.34
	2.97	5.92	...	...
	3.63	...	6.56	2.34
	4.95	5.75	...	...
	5.45	...	6.61	2.36
	6.93	5.70	...	...
	7.26	...	6.60	...
(b)	Nil	7.53†	...	...
	3.60	7.02†	...	...
	6.00	6.84†	...	...
	8.40	6.52†	...	...

† $10^4 k_{1s}^{-1}$ in presence of initially added chloride [Cl⁻]: 0.053 M

Solvent: 50% HOAc-50% H₂O (v/v) Temp.: 40° C [HClO₄]: 0.1 M

[CBT]: 3.15×10^{-3} M [*Acetone]: 3.29×10^{-2} M

** [Ethylmethylketone]: 3.25×10^{-3} M; *** [Acetophenone]: 3.23×10^{-2} M

(a) in the absence of Cl⁻; (b) in presence of Cl⁻

Table 10. First order rate constants and activation parameters for the Chlorination of ketones by CBr in 50% HOAc-50%

Substrate	$10^3 k_1' \text{ s}^{-1}$						(ii)	(iii)
	30° C	35° C	40° C	45° C	50° C	(i)		
Acetone	9.79	17.1	19.9	41.0	61.1	17.8	17.2	-25.2
Acetone- d_6	0.94	11.70	3.01	5.58	...	22.5	21.8	-14.2
Ethylmethyl ketone	6.89	12.2	25.4	46.0	...	24.3	23.7	-3.97
Isobutyl methyl ketone	4.80	8.19	20.3	38.1	...	26.5	25.9	+2.66
3,3-dimethyl but-2-one	3.87	6.70	11.4	20.0	...	20.8	20.2	-16.7
Acetophenone	2.63	4.42	7.60	13.2	21.4	21.1	20.5	-16.2
<i>p</i> -chloroacetophenone	2.40	4.00	6.37	10.2	...	18.4	17.8	-25.6
<i>m</i> -chloroacetophenone	1.56	2.68	4.45	7.76	...	19.7	16.1	-13.8
<i>p</i> -Nitroacetophenone	1.14	...	3.30	5.62	9.35	21.1	20.4	-18.5
<i>m</i> -Nitroacetophenone	1.02	2.71	4.68	7.82	...	21.4	20.8	-17.8
<i>p</i> -Methyl acetophenone	3.42	5.97	10.9	19.5	...	21.6	21.0	-14.8
<i>p</i> -Acetylacetophenone	3.63	6.20	10.3	17.0	...	19.6	19.0	-20.9
Propiophenone	1.49	...	3.34	4.63	7.14	15.4	14.8	-36.6
Cyclopentanone	13.7	23.0	47.3	81.6	...	26.1	25.5	+2.91
Cyclohexanone	48.8	82.3	129	207	...	18.3	17.7	-19.9
Cycloheptanone	18.93	15.5	25.7	43.8	...	20.3	19.6	-17.0
Cyclooctanone	77.2	120	212	334	...	19.0	18.4	-16.8

(i) E_{aa} (kcal mol⁻¹) (ii) $\Delta H^\ddagger$ (kcal mol⁻¹) (iii) $\Delta S^\ddagger$ (kcal deg⁻¹ mol⁻¹) (iv) $\Delta G^\ddagger$ (kcal mol⁻¹)

Table 11. Effect of added sodium chloride.

[Substrate] 10^2 M	[NaCl] 10^2 M	$10^4 k_1 s^{-1}$
(a) Acetone :		
3.25	10.9	9.21
3.25	8.70	8.13
3.25	5.30	7.53
2.68	5.30	66.65
4.02	5.30	8.61
4.69	5.30	9.08
(b) Acetone- d_6 :		
3.19	5.30	4.00
3.83	5.30	4.21
4.47	5.30	4.56
(c) Ethylmethyl ketone :		
3.25	10.9	10.7
3.25	8.70	9.81
3.25	5.30	9.17
3.25	2.20	6.11
2.60	5.30	7.90
3.91	5.30	9.45
(d) Acetophenone :		
3.20	8.00	7.07
3.20	5.30	5.99
3.20	2.00	4.03
2.52	5.30	5.13
4.40	5.30	6.74

Solvent : 50% HOAc-50% H_2O (v/v) ; $[HClO_4]$: 0.1 M Temp. : 40° C

[CBT] : 3.32×10^{-3} M

k_1 is the first order rate constant for the disappearance of CBT.

4.8 Effect of added chloride on rate in mineral acid medium

Initially added chloride, apart from enhancing the rate, changes the rate law itself. In the presence of chloride the order with respect to [CBT] changes to unity (it is zero in the absence of chloride) and that with respect to [ketone] becomes fractional (0.6 for acetone). The dependence on the concentration of chloride itself is fractional (0.3) (table 11). The order on acetone and chloride were obtained respectively from plots of $\log k_1$ vs $\log$ [acetone] and $\log k_1$ vs $\log [Cl^-]$, where k_1 stands for the rate constant for the first order loss of CBT in the presence of added chloride.

4.9 Effect of added sodiumacetate on rate

While the reaction is extremely sluggish in the absence of acetate, its addition in

Table 12. Effect of added Sodium acetate.

[Substrate] 10^2 M	[NaOAc] 10^2 M	$10^8 k_0$ mol l^{-1} s $^{-1}$
(a) Acetone :		
3.20	Nil	6.30
3.20	80.0	29.2
3.20	40.0	19.8
3.20	20.0	14.2
3.20	2.54	9.8
3.99	2.54	11.9
4.99	2.54	14.7
(b) Acetophenone :		
3.15	Nil	3.98
3.15	2.55	5.47
3.15	7.65	6.55
3.15	5.10	7.88
3.78	5.10	7.89
4.40	5.10	9.31
2.52	5.10	5.32

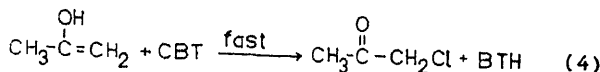
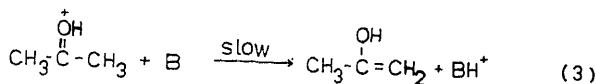
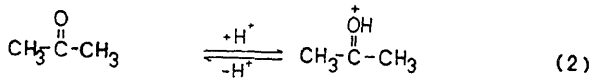
Solvent : 50% HOAc-50% H₂O (v/v) ; Temp. : 40° C [CBT] : 3.20×10^{-3} M

order with respect to ketone and zero order with respect to CBT. There is, however, a fractional order dependence (0.30-0.50) on [acetate], for the halogenation of acetone and acetophenone (table 12). The order on [acetate] has been obtained from a plot of $\log k_0$ vs $\log$ [acetate].

4.10 Mechanism of halogenation in the absence of chloride

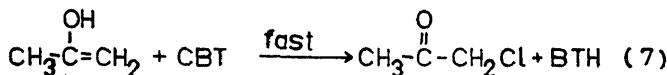
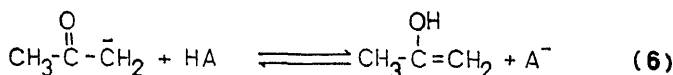
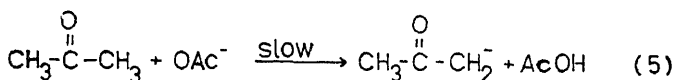
4.10a: The halogenation of ketones by molecular halogen is usually catalysed both by acids and bases. However, the reaction between ketones and CBT could not be studied under alkaline conditions due to solubility limitations. The rate law under acidic conditions is given by equation (1). The zero order on the halogenating agent is in conformity with the usual kinetic picture namely a slow rate-determining formation of the enol followed by a fast attack of the halogenating species. This rate of attack is faster than the rate at which the enol reverts to the ketone. The catalysis by acids is ascribed to the preequilibrium "Proton transfer" shown in scheme I. The enhanced rate encountered in the case of HCl could be attributed to a cumulative and concurrent catalysis by both H⁺ and Cl⁻ (However, the addition of Cl⁻ alters the kinetic picture).

That the enolisation of the ketone is rate-determining in these reactions is corroborated by the fact that there is a primary kinetic isotope effect of magnitude 6.6 (for acetone and acetone-d₆). Similar effects have been reported (Balakrishna and Thiagarajan, 1972) in the halogenation of ketones with other



SCHEME I

(B = Base ; CBT = 1-chlorobenzotriazole ; BTH = Benzotriazole)



SCHEME II

HA = Acid

The enolisation of ketones has been shown to be a general acid-base catalysed reaction (Bell 1973). In acetic acid-acetate buffer systems, the catalysis by both acetate and acetic acid have to be taken into account. The generalised rate expression of the form

$$\text{rate} = \{k_{\text{H}_2\text{O}} [\text{H}_2\text{O}] + k_{\text{H}^+} (\text{H}^+) + k_{\text{OH}^-} [\text{OH}^-] + k_{\text{HOAc}} [\text{HOAc}] + k_{\text{OAc}^-} [\text{OAc}^-]\} [\text{Ketone}] \quad (8)$$

has been reported (Dawson and Spirey 1930 ; Bell and Jones 1953) for such a situation.

Assuming a general acid-base catalysed enolisation for the chlorination of ketones by CBT, by the proper choice concentrations of catalysing species and by a regression analysis of the rate data using a micro 2200 Hindustan Computer, the catalytic coefficients have been calculated. The following approximations

ion are negligible and remain constant throughout and (ii) from the pH value of the buffered solutions, the $[\text{OAc}^-]$ may be calculated using the K_a value for HOAc to be valid in such high concentrations of acetic acid.

k_{H^+} was first evaluated using rate constants at high $[\text{H}^+]$ where it may be assumed that catalysis by H^+ would be the predominant one. Employing these k_{H^+} values and the rates in buffered HOAc- H_2O media, k_{OAc^-} was evaluated. Utilising the value of k_{H^+} and k_{OAc^-} and the rate data for the variation of HOAc in the solvent media k_{HOAc} was evaluated. This procedure was repeated several times from k_{H^+} onwards, by correcting for the catalysis of OAc^- and HOAc in acid media, until two successive determinations gave reproducible values. Thus,

$$\text{rate} = \{k' [\text{C}] + 4.48 \times 10^{-6} [\text{H}^+] + 1.68 \times 10^{-7} [\text{OAc}^-] + 9.09 \times 10^{-9} [\text{HOAc}]\} [\text{Ketone}] \quad (9)$$

where $k' [\text{C}]$ represents the total contribution of OH^- and solvent water. It may be noticed that the values of the calculated catalytic coefficients are comparable to those obtained by earlier workers (Bell and Jones 1953). The rate law reported by Bell and Jones is

$$\text{rate} = \{8.33 \times 10^{-13} [\text{H}_2\text{O}] + 2.68 \times 10^{-6} [\text{H}^+] + 2.5 \times 10^{-2} [\text{OH}^-] + 8.33 \times 10^{-8} [\text{HOAc}] + 2.50 \times 10^{-7} [\text{OAc}^-]\} [\text{Ketone}] \quad (10)$$

The high value for the catalytic coefficient of H^+ point to the fact that at high acidities the second term in equation (9) is dominant, accounting for the observed first order dependence on $[\text{H}^+]$. Any increase in $[\text{OAc}^-]$ is accompanied by a gradual and corresponding decrease in $[\text{H}^+]$. The fractional order obtained on $[\text{OAc}^-]$ may be due to the combination of the two effects *viz* an enhanced catalysis by OAc^- and an opposing reduction in the catalysis by H^+ by concentration effects.

The chlorinating species reacting with the enolic form of the ketone could be either CBT itself or species derived from it like CBT H^+ , Cl^+ , HOCl , $\text{H}_2\text{O}^+\text{Cl}$ and ClOAc . However, in view of the independence of rate on the initial concentration of CBT these species become kinetically indistinguishable.

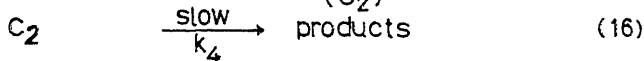
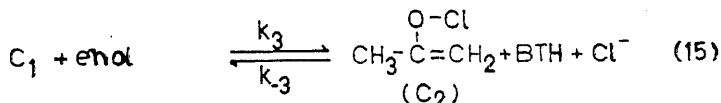
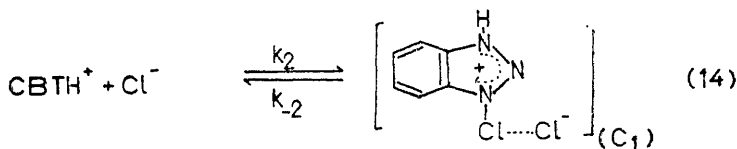
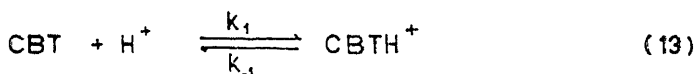
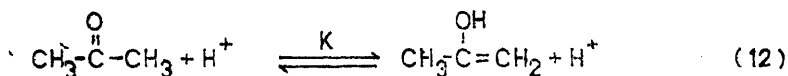
4.10b. Structural effect: As the rate is dependent only on the rate of enolisation under these conditions, any change in rate could be attributed only to the ease or otherwise of enolisation. For example, in the case of alicyclic ketones, it is noticed (table 7) that those with odd number of carbon atoms get chlorinated slower than those with even number. It has been reported that alicyclic ketones with even number of carbon atoms have a greater enolic content than their adjacent analogues with odd number of carbon atoms (Gero 1961; Alinger *et al* 1967) though reports contrary to this have also been made indicating that the enol of cyclohexanone, for example is less stable than that of cyclopentanone (Bell and Smith 1966; Hine 1975).

in the transition state. However, since the present reaction involves a protonation followed by a deprotonation, the ρ value results only from the overall contribution by the substituents to these opposing processes. A value of $\rho = -0.6$ has been reported for the bromination of substituted benzyl phenyl ketones.

4.10c. *Mechanism of halogenation in the presence of chloride ions* : It is significant to point out that the rate law, in the presence of chloride ions, is

$$-\frac{d[\text{CBT}]}{dt} = k' [\text{CBT}] [\text{H}^+] [\text{acetone}]^{0.6} [\text{Cl}^-]^{0.2} \quad (1)$$

This might mean that CBT and Cl^- interact to produce a steady and small concentration of another halogenating species (C_1), which then interacts with the substrate in its enolic form to give the products *via* a complex (C_2) *viz* the enol hypochlorite (scheme 3) (For acetone- d_6 under these conditions the kinetic picture is retained except for a lowered order dependence on the substrate)



SCHEME III

(Note : The k_2 in equation 14 is different from the one given in equation 1)

From scheme 3,

$$\text{Rate} = k_4 [\text{C}_2] \quad (1)$$

applying steady state approximation to (C_1) and (C_2)

$$[C_2] = \frac{k_2 k_3 [\text{enol}] [\text{CBTH}^+] [\text{Cl}^-]}{\{k_4 + k_{-3} [\text{BTH}] [\text{Cl}^-]\} \{k_{-2} + k_3 [\text{enol}] - \{k_3 [\text{enol}] \times k_{-3} [\text{BTH}] [\text{Cl}^-]\}} \quad (19)$$

$$\text{Rate} = \frac{k_2 k_3 k_4 [\text{enol}] [\text{CBTH}^+] [\text{Cl}^-]}{k_{-2} k_4 + k_3 k_4 [\text{enol}] + k_{-2} k_{-3} [\text{BTH}] [\text{Cl}^-]} \quad (20)$$

This equation predicts fractional order dependences for rate on both [ketone] and [Cl⁻] and a first order dependence on [CBT], all of which have been realised [rate law as per equation (11)]. There is a definite but small retardation with added benzotriazole (table 9, b) which is also in consonance with equation (20).

Further as per (20), the reciprocal of rate should be linearly related to (i) the reciprocal of [enol] when [CBT], (H⁺), (Cl⁻) and (BTH) are not varied and (ii) the reciprocal of [Cl⁻] when [CBT], [H⁺], [enol] and [BTH] are not varied. This has been tested out by plotting 1/k₁ vs 1/[enol] (c.c. = 0.999) as also 1/k₁ vs 1/Cl⁻ (c.c. = 0.999); both are linear with clear Y-intercepts which also indicates "Complex formation" (the chlorination of acetone-d₆ by CBT in the presence of chloride is also first order in CBT but exhibits a fractional order dependence (0.3) on [acetone-d₆]). Similar results have been obtained (Balasubramanian 1976) in the chlorination of acetone-d₆ by chloramine-T. A plot of 1/k₁ vs 1/[acetone-d₆] also yields a straight line with a clear Y-intercept (c.c. = 0.976). The k₁ involved in the above plots is the rate constant for the first order disappearance of CBT.

Acknowledgements

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Isocoumarins : Part 7. New synthesis of 3-phenyl-3,4-dihydroisocoumarins and their antifungal activity

B H BHIDE* and R C SHAH

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar 388 120, India

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Abstract. *o*-Lithio-N-methylbenzamides upon condensation with styrene oxide give corresponding 3-phenyl-3,4-dihydroisocoumarins. The antifungal activity of the compounds has been tested.

Keywords. *o*-Lithio-N-methylbenzamides ; 3-phenyldihydroisocoumarins ; antifungal activity.

1. Introduction

The dihydroisocoumarins having C₃-phenyl group are quite common in nature, e.g., Phyllostulcin (Henri and Gilbert 1977), Homalycin (Govindachari *et al* 1975) and Hydrangenol (Ibrahim and Towers 1962) etc. There are a few methods for the synthesis of 3-phenyl-3,4-dihydroisocoumarins (Brown *et al* 1975 ; Nizamuddin and Ghosal 1974 ; Usgaonkar 1971 ; Naoi *et al* 1976 ; Tobinga and Akiteru 1971). However these methods comprise several steps and have no general applicability. Hence it seemed desirable to explore a simple and general method for synthesising 3-phenyl-3,4-dihydroisocoumarins.

The N-methylbenzamides are known to undergo lithiation at ortho positions and these *o*-lithio-N-methyl benzamide upon alkylation with epoxides give dihydroisocoumarins (Bhide and Shah 1980 ; Bhide and Brahmhatt 1980). In the present work *o*-lithio-N-methylbenzamides have been condensed with styrene oxide to give 3-phenyl-3,4-dihydroisocoumarins.

2. Results and discussion

The condensation of *o*-lithio-N-methylbenzamide, 2- and 4-methoxy-N-methylbenzamide, 3,4-dimethoxy-N-methylbenzamide, 3,4,5-trimethoxy-N-methylbenzamide and 4-methyl-N-methylbenzamide with styrene oxide gave after hydrolysis

* To whom correspondence should be made.

corresponding 3-phenyl-3, 4-dihydroisocoumarins (I-VI) respectively. Besides dihydroisocoumarins, the alkylation reaction also gave a side product having m.p. 95°C. It was identified as α,β -diphenyl- γ -butyrolactone (VII) on the basis of spectral and analytical evidences. It has been reported (Shinsuke *et al* 1970) that styrene oxide isomerizes to (VII) when treated with a catalyst like lithium benzoynickel carbonate, lithium-*p*-toluoylnickel carbonate etc. This suggested that the *o*-lithio-N-methylbenzamides probably bring about the isomerization of styrene oxide to (VII). This side reaction could be a possible reason for the poor yields of the dihydroisocoumarins in the present work.

2.1. Antifungal activity of 3-phenyl-3,4-dihydroisocoumarins

The 3-phenyl dihydroisocoumarins possess antifungal activity (Nakajima *et al* 1979; Maaakwa and Yoshikawa 1978). Hence the present compounds were screened for antifungal activity by modified paper disc assay (Sharvelle 1960) using different fungi. The testing was carried out in the DMF solution at different concentrations as it was innocuous. The petri dishes were incubated in the uv chamber at room temperature for 4-7 days and examined for the fungal growth on filter-paper.

Compounds I, II and V showed good fungicidal activity against *A. niger*, *Curvularia fusarium* and *Rhizopus* while compounds III, IV and VI showed slight fungicidal activity against *Fusarium*, *Rhizopus*, *Rhizoctonia helminthosporium* and *Alternaria cotton*.

3. Experimental

3.1. Preparation of all N-methylbenzamides

This was described in the earlier papers in this series.

3.2. Lithiation and condensation of *o*-lithio derivatives with styrene oxide :

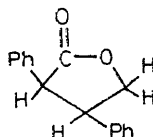
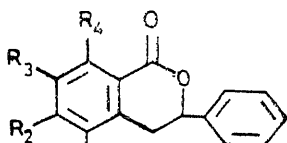
The following general procedure was used. To a well-stirred solution of N-methylbenzamides (0.037 mol) in dry THF (75 ml) was added at room temperature *n*-BuLi (0.30 mole) in dry ether under nitrogen atmosphere for 10 min. The

I. $R_1 = R_2 = R_3 = R_4 = H$. II. $R_1 = R_3 = R_4 = H$, $R_2 = OMe$.

III. $R_1 = R_2 = R_3 = H$, $R_4 = OMe$.

IV. $R_1 = R_2 = OMe$, $R_3 = R_4 = H$. V. $R_1 = R_2 = R_3 = OMe$, $R_4 = H$.

VI. $R_1 = R_3 = R_4 = H$, $R_2 = Me$.



under nitrogen atmosphere at reflux temperature for 45 min and alkaline hydrolysis work up as before (Narasimhan and Bhide 1971) gave the following 3-phenyl 3,4-dihydroisocoumarins (I-VI) and VIII.

3.2a. 3-Phenyl-3,4-dihydroisocoumarin (I): White needles, crystallised from ethylacetate-hexane, yield 8%, m.p. 89–90° (found: C, 80.24; H, 5.13; $C_{15}H_{12}O_2$ requires C, 80.37; H, 5.35%); IR (KBr): 1720 cm^{-1} (δ lactone); UV (95% ethanol): 240, 257 nm ($\log \epsilon$ 4.0, 3.65); NMR ($CDCl_3$): δ 3.15 (2H, complex, benzylic $-CH_2-$), 5.55 (4 lines, H_3 proton $J_{Ar} = 4Hz$, $J_{Bs} = 12Hz$), 7.60 (8H, complex, aromatic protons), 8.1 (1H, complex, H_8 proton).

3.2b. 6-Methoxy-3-phenyl-3,4-dihydroisocoumarin (II): White needles, crystallised from ether-hexane, yield 5%; m.p. 115–16° (found: C, 75.16; H, 5.86; $C_{16}H_{14}O_3$ requires C, 75.60; H, 5.50%); IR (KBr): 1710 cm^{-1} (δ lactone); UV (95% ethanol): 251, 293 nm ($\log \epsilon$ 4.2, 3.77); NMR ($CDCl_3$): δ 3.0 (2H complex, benzylic $-CH_2-$), 3.6 (3H, singlet $-OCH_3$ group), 5.2 (4 lines, H_3 proton, $J_{Ar} = 4Hz$, $J_{Bs} = 12Hz$), 6.1–7.0 (7H, complex, aromatic protons), 7.55 (1H, doublet, $J_0 = 8Hz$, H_8 proton).

3.2c. 8-Methoxy-3-phenyl-3,4-dihydroisocoumarin (III): White needles, crystallised from ether-hexane, yield 30%; m.p. 151° (found C, 75.49; H, 5.76; $C_{16}H_{14}O_3$ requires C, 75.60; H, 5.76; IR (KBr): 1745 cm^{-1} (δ lactone); UV (95% ethanol): 305, 350 nm ($\log \epsilon$ 4.0, 3.90); NMR ($CDCl_3$) δ 3.1 (2H, complex, benzylic $-CH_2-$), 3.85 (3H, singlet $-OCH_3$ group), 5.30 (4 lines, H_3 proton, $J_{Ar} = 4Hz$, $J_{Bs} = 12Hz$), 6.7–7.5 (8H, complex, aromatic protons).

3.2d. 5,6-Dimethoxy-3-phenyl-3,4-dihydroisocoumarin (IV): White needles, crystallised from ether-hexane, yield 10%; m.p. 127° (found: C, 71.46; H, 6.00; $C_{17}H_{16}O_4$ requires C, 71.82; H, 5.63%); IR (KBr): 1715 cm^{-1} (δ lactone); UV (95% ethanol) 221, 266 nm ($\log \epsilon$ 4.83, 4.33), NMR ($CDCl_3$): δ 3.2 (2H, 8 lines,

$$\begin{array}{c} -O \\ | \\ -Ar-CH_2-\overset{\overset{O}{\parallel}}{C}-Ph \end{array}$$

the AB part of an ABx system, $J_{AB} = 16Hz$, $J_{Ar} = 4Hz$, $J_{Bs} = 11Hz$, 3.75 and 3.9 (6H, two singlets, two $-OCH_3$ groups) 5.4 (4 lines, H_3 proton, $J_{Ar} = 4Hz$, $J_{Bs} = 12Hz$), 6.9 (1H, doublet, $J = 8Hz$, H_7 proton, 7.0–7.5 (7H, complex, aromatic protons), 7.85 δ (1H, doublet, $J = 8Hz$, H_8 proton).

3.2e. 5,6,7-Trimethoxy-3-phenyl-3,4-dihydroisocoumarin (V): White needles, crystallised from ether-hexane, yield 9%; m.p. 111° (found C, 68.56; H, 5.43; $C_{18}H_{18}O_5$ requires C, 68.80; H, 5.73%); IR (KBr): 1730 cm^{-1} (δ lactone); UV (95% ethanol): 224, 259 nm ($\log \epsilon$ 3.90, 3.40); NMR ($CDCl_3$): δ 3.0 (2H, 8 lines, the AB part of an ABx system, $J_{AB} = 17Hz$, $J_{Ar} = 5Hz$, $J_{Bs} = 12Hz$,

$$\begin{array}{c} -O \\ | \\ -Ar-CH_2-\overset{\overset{O}{\parallel}}{C}-Ph \end{array}$$

Ar- $\overset{\overset{O}{\parallel}}{C}$ -Ph), 3.6, 3.7 and 3.8 (9H, three singlets, three $-OCH_3$ groups), 5.3 (4 lines, H_3 proton, $J_{Ar} = 4Hz$, $J_{Bs} = 12Hz$, 6.1–6.8 (5H, complex, aromatic protons), 7.2 (1H, singlet, H_8 proton).

3.2f. 6-Methyl-3-phenyl-3, 4-dihydroisocoumarin (VI) : White needles, crystallised from ether-hexane, yield 7%, m.p. 96° (found : C, 80.56, H, 5.54 ; $C_{16}H_{14}O_2$ requires C, 80.67 ; H, 5.88) ; IR (KBr) : 1725 cm^{-1} (ν lactone), UV (95% ethanol) ; 240, 257 nm ($\log \epsilon$ 4.0, 3.65), NMR ($CDCl_3$) δ 2.4 (3H, singlet, $-CH_3$ protons), 3.15 (2H, complex, benzylic $-CH_2-$), 5.55 (4 lines, H_3 protons, $J_{As} = 4Hz$, $J_{Bs} = 12Hz$) 7.40 (7H, complex, aromatic protons) 8.08 (1H, doublet $J_0 = 8Hz$, H_8 proton).

3.2g. α,β -Diphenyl- γ -butyrolactone (VII) : White needles, crystallised from ether-hexane, yield 10% ; m.p. 95° (found : C, 80.48 ; H, 5.68 ; $C_{16}H_{14}O_2$ requires C, 80.64 ; H, 5.92%), IR (KBr) : 1780 cm^{-1} (ν lactone) ; UV (95% ethanol) 250, 310 nm ($\log \epsilon$ 4.50, 3.45), NMR ($CDCl_3$) : δ 3.95 (2H, $-CH_2-$ group), 4.2-4.8 (2H, complex), 7.3 (10H, complex, aromatic protons).

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A general synthesis of thiazoles. Part 4¹. Synthesis of 5-acyl-2, 4-diaminothiazoles²

S RAJAPPA*, V SUDARSANAM**, V G YADAV and
B V GAIKWAD

CIBA-GEIGY Research Centre, Goregaon, Bombay 400 063, India

** The Boots Company (India) Ltd., SION, Bombay 400 022, India

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Abstract. N,N,N',N'-tetramethylguanidine has been added to methyl and phenyl isothiocyanates. Reaction of the adducts with α -haloketones has yielded 5-acyl-2- (substituted) amino-4-dimethylaminothiazoles.

Keywords. 5-Acyl-2-amino-4-dimethylaminothiazoles.

1. Introduction

In 1970, we had reported the first example of a novel thiazole synthesis (Rajappa and Advani 1970). In this synthesis, a functionalized thiourea derivative provided two ring carbon atoms and both the hetero atoms of the resultant thiazole ; the remaining carbon atom (C-5) was supplied by the methylene group of an α -halo-ketone. The synthesis can be schematically expressed as shown in scheme 1. The requisite thiourea derivative was obtained by addition of an amidine to an isothiocyanate. During the subsequent cyclization, the amine HNRR was eliminated (scheme 2). We have also reported on the use of iminoethers as starting materials instead of amidines ; in this case, an alcohol is eliminated at the cyclization stage (Rajappa *et al* 1979).

We have now systematically investigated the possible variations in the substitution pattern of the thiazole. The results are reported in this and in the following papers. The present paper concerns itself with the introduction of a dimethylamino group at position 4 ; the following papers are devoted to the possible changes at positions 2 and 5 of the thiazole.

* To whom correspondence should be made.

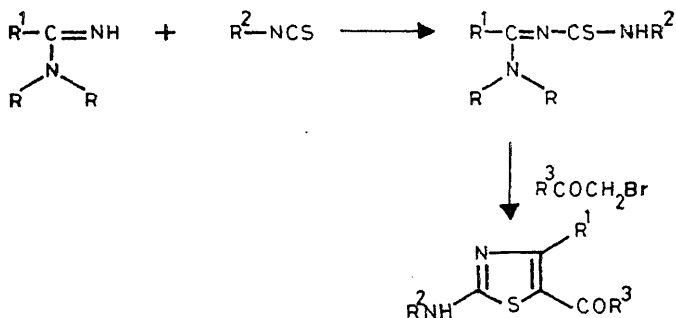
¹ Part 3. Rajappa *et al* 1979.

² Contribution No. 673 from CIBA-GEIGY Research Centre.

Scheme 1



Scheme 2



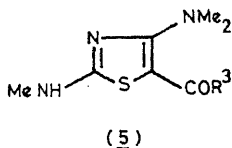
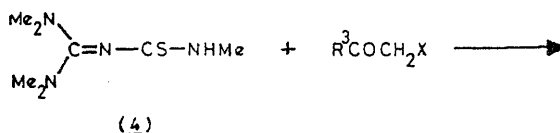
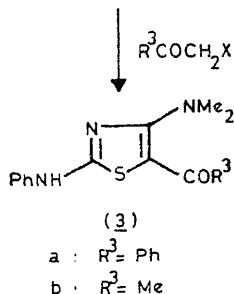
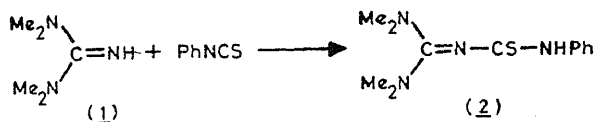
2. Results and discussion

As shown in scheme 2, the synthesis utilizing an amidine-isothiocyanate adduct would invariably lead to thiazoles bearing an alkyl or aryl group at position 4. It is obvious that the use of a guanidine instead of an amidine in the above sequence would lead to thiazole derivatives with an amino group at that position. In order to eliminate the ambiguities associated with an unsymmetrical guanidine, we chose to use tetramethylguanidine 1 as our substrate. Reaction of this with phenyl isothiocyanate gave the adduct 2. Condensation of this with α-haloketones has provided us with 5-acyl-2-anilino-4-dimethylaminothiazoles 3 in good yield. Similarly, reaction of tetramethylguanidine with methyl isothiocyanate gave adduct 4, which led to the 5-acyl-4-dimethylamino-2-methylaminothiazoles 5 with α-haloketones.

The same concept has recently been utilized to generate 5-benzoyl-2,4-diaminothiazoles by Rajasekharan and Sulekha (1981).

3. Experimental

Melting points are uncorrected. ¹H NMR spectra were recorded on a Varian EM 360L spectrometer. Chemical shifts are expressed in δ values (ppm) downfield from TMS. Mass spectra were determined on a Varian Mat CH7 instrument.



- a : $\text{R}^3 = \text{Me}$
 b : $\text{R}^3 = \text{Ph}$
 c : $\text{R}^3 = 4\text{-BrC}_6\text{H}_4\text{-}$

1. Addition of tetramethylguanidine to isothiocyanates

solution of phenyl isothiocyanate (13.5 g) in isopropanol (40 ml) was cooled 0–5° and treated dropwise with stirring with a solution of tetramethyl-guanidine (2.7 g) in isopropanol (40 ml). Stirring was continued for 2½ hr at this temperature and then for 1 hr at 30°. The solid was filtered and recrystallized from isopropanol to give the adduct (3) (23.5 g), m.p. 186° (Found : C, 57.88 ; H, 3.37 ; N, 22.49. $\text{C}_{12}\text{H}_{18}\text{N}_4\text{S}$ requires C, 57.58 ; H, 7.25 ; N, 22.39%). NMR (MSO-d_6) : 2.9 (s, 4Me) ; 6.8 to 7.6 (m, 5 Ar-H). MS : 250 (M^+).

A solution of methyl isothiocyanate (4 g) in isopropanol (10 ml) was similarly treated with tetramethylguanidine (6 g) in isopropanol (20 ml). The solution was left at 30° for 16 hr and then warmed at 70° for 1½ hr. The solvent was then removed *in vacuo* and the residue recrystallized from chloroform-hexane to give the adduct (4) (7 g), m.p. 159–161° (Found : C, 44.99 ; H, 8.81 ; N, 29.53,

3.2. Condensation of the adducts with α -haloketones

The adduct (2) (5 g) was stirred and refluxed in isopropanol (350 ml) with phenacyl bromide (4.4 g) for 5 hr. The solvent was then removed *in vacuo*, the residue left in cold water for 3 hr and the yellow solid filtered. This was basified with KHCO_3 solution and extracted with ethyl acetate. The solution was dried and evaporated. The product was crystallized from ethanol to give 2-anilino-5-benzoyl-4-dimethylaminothiazole (3a) (5.7 g), m.p. 128° (Found: C, 63.66; H, 5.85; N, 12.45. $\text{C}_{18}\text{H}_{17}\text{N}_3\text{OS} \cdot \text{H}_2\text{O}$ requires C, 63.33; H, 5.61; N, 12.31%). NMR (CDCl_3): 3.07 (s, 2Me); 6.8 to 7.8 (m, 10 ArH). MS: 323 (M^+).

The adduct (2) (3.45 g) was similarly condensed with chloracetone (2 ml) in isopropanol (270 ml). After refluxing for 6 hr, the product was worked up as above to give 5-acetyl-2-anilino-4-dimethylaminothiazole (3b) (2.3 g), m.p. 156 – 158° (from ethyl acetate–toluene) (Found: C, 59.73; H, 6.10; N, 16.22. $\text{C}_{13}\text{H}_{15}\text{N}_3\text{OS}$ requires C, 59.76; H, 5.79; N, 16.08%). NMR ($\text{CDCl}_3 + \text{DMSO}-d_6$): 2.25 (s, Me); 3.13 (s, 2Me); 6.8 to 7.7 (m, 5 ArH). MS: 261 (M^+).

A mixture of the adduct (4) (2 g) and chloracetone (1 g) in isopropanol (25 ml) was refluxed for 6 hr and the solvent then removed *in vacuo*. The residue was cooled, basified and extracted with ethyl acetate. The organic extract was dried and evaporated. The product was crystallized from ethyl acetate–ether to give 5-acetyl-4-dimethylamino-2-methylaminothiazole (5a) (0.75 g), m.p. 150 – 151° . (Found: C, 48.58; H, 6.76; N, 21.03. $\text{C}_8\text{H}_{13}\text{N}_3\text{OS}$ requires C, 48.23; H, 6.58; N, 21.10%). NMR (CDCl_3): 2.17 (s, Me); 3.05 (s, 2Me); 3.47 (s, Me). MS: 199 (M^+).

The adduct (4) (2 g) was refluxed in isopropanol (25 ml) for 6 hr with phenacyl bromide (2.1 g). The solution was cooled and filtered. The solid was basified with KHCO_3 solution and the base recrystallized from ethanol to give 5-benzoyl-4-dimethylamino-2-methylaminothiazole (5b) (1.8 g), m.p. 203° . A further small quantity of the product was obtained from the isopropanol filtrate (Found: C, 60.00; H, 6.07; N, 15.76. $\text{C}_{13}\text{H}_{15}\text{N}_3\text{OS}$ requires C, 59.76; H, 5.79; N, 16.08%). NMR ($\text{DMSO}-d_6$): 2.8 (d, Me); 3.0 (s, 2Me); 7.4 to 7.8 (m, 5 ArH); 8.32 (q, NH). MS: 261 (M^+).

A similar reaction of the adduct (4) with *p*-bromo-phenacyl bromide gave the thiazole (5c), m.p. 209° (Found: C, 46.09; H, 4.43; N, 12.14. $\text{C}_{13}\text{H}_{14}\text{BrN}_3\text{OS}$ requires C, 45.90; H, 4.15; N, 12.35%). NMR ($\text{DMSO}-d_6$): 2.75 (d, Me); 2.93 (s, 2Me); 7.3 to 7.7 (4ArH); 8.37 (q, NH). MS: 339, 341 (M^+).

Acknowledgement

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A general synthesis of thiazoles. Part 5¹. Synthesis of 5-acyl-2-dialkylaminothiazoles²

S RAJAPPA*, V SUDARSANAM**, B G ADVANI and
A V RANE

CIBA-GEIGY Research Centre, Goregaon, Bombay 400 063, India

** The Boots Company (India) Ltd., SION, Bombay 400 022, India

MS received 12 August 1982

Abstract. Amidinothioureas (7), (11) and (12) obtained by condensation of N,N-disubstituted thioureas with amide acetals have been used as starting materials for the synthesis of thiazoles. Thus, reaction with chloracetone and phenacyl bromides leads to ketones; the use of chloracetic ester in this reaction yields the thiazole-5-carboxylic ester (10).

Keywords. 5-Acyl-2-dialkylaminothiazoles; 2-morpholinothiazole-5-carboxylic ester.

1. Introduction

In the original version of the novel synthesis of thiazoles that we have developed (Rajappa and Advani 1970), the adduct (1) of an amidine and an isothiocyanate is condensed with an α -haloketone (scheme 1). Such an approach restricts the 2-substituent to RNH.

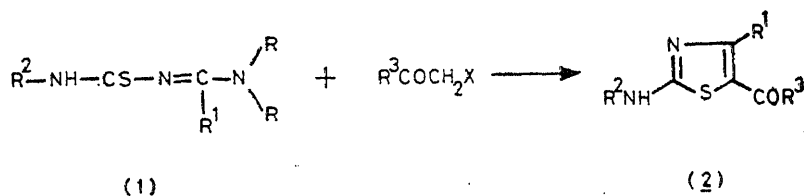
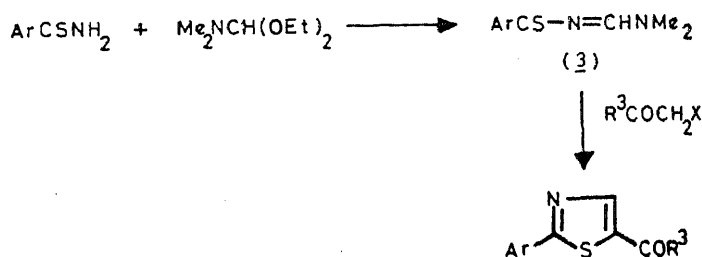
Subsequent to our publication, but seemingly unaware of our work, Meslin and Quiniou (1975) described a related synthesis of 2-aryl-5-acyl thiazoles. They utilized as their starting material, the condensation product 3 of an aromatic thioamide with DMF acetal (scheme 2). This route was later extended by the Lederle group (Lin *et al* 1979) to prepare 2-aminothiazoles of type 2, again without reference to our prior work. They condensed N-monosubstituted thioureas with amide acetals to give compounds similar to (1), and then reacted these with α -haloketones.

One of our objectives in this area was to devise a viable route to 5-acyl-2-aminothiazoles (4) in which the exocyclic nitrogen at position 2 carries two substituents (or represents a cyclic amine). One approach to this problem is through the use of acyl thioureas (5) (scheme 3) (Liebscher and Hartmann 1974).

* To whom correspondence should be made.

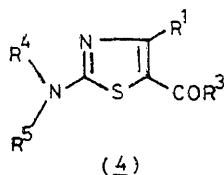
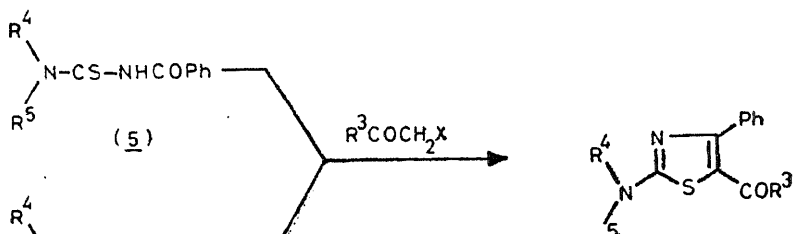
¹ Part 4. Preceding paper (Rajappa *et al* 1982).

² Contribution No. 674 from CIBA-GEIGY Research Centre.

Scheme 1Scheme 2

Another precursor which would lead to the desired product is the adduct (6) of a secondary amine and an imidoyl isothiocyanate (Ried and Kaiser 1976) (scheme 3).

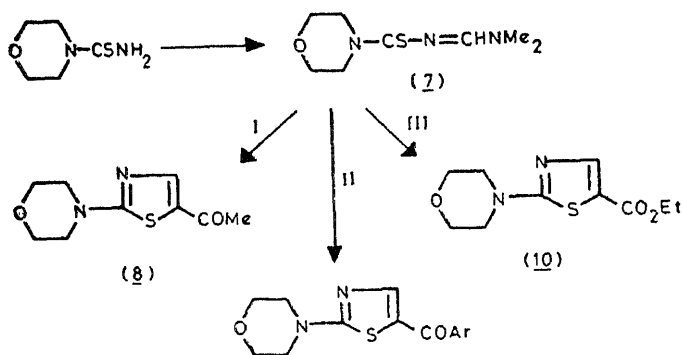
We now find that the condensation products of N, N-disubstituted thioureas with amide acetals form convenient starting materials for the synthesis of thiazoles of type (4).

Scheme 3

Thiocarbamoylmorpholine condensed with DMF acetal to give the formamidine derivative (7). This reacted with a variety of α -halo carbonyl compounds as shown in scheme 4. Thus the thiazolyl ketones 8 and 9a were derived by reaction with chloroacetone and phenacyl bromide respectively. Interestingly, even the thiazole-5-carboxylic ester (10) could be produced from (7) by reaction with chloroacetic ester.

The related 1-thiocarbamoyl-4-methylpiperazine was also reacted with both DMF acetal and DMA acetal to give the amidine derivatives (11) and (12) (scheme 5).

Scheme 4



(9) a: Ar = Ph

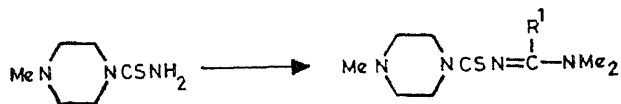
b: Ar = 4-Cl-3-NO₂-C₆H₃

I: ClCH₂COCH₃

II: ArCOCH₂Br

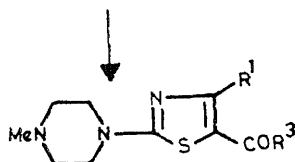
III: ClCH₂CO₂Et

Scheme 5



(11) R¹ = H

(12) R¹ = Me



(13) R¹ = H; R³ = 4-NO₂-C₆H₄

(14) R¹ = H; R³ = 3-NO₂-C₆H₄

Thiazoles (13 to 16) were obtained by condensation of these with the appropriate phenacyl bromides.

3. Experimental

Melting points are uncorrected. ^1H NMR spectra were recorded either on a Varian A 60 or a Varian EM 360 L spectrometer. Chemical shifts are expressed in δ values (ppm) downfield from TMS. Mass spectra were determined on a Varian Mat CH 7 instrument at 70 eV utilizing direct insertion.

3.1. Synthesis of 2-morpholinothiazoles

A mixture of N-thiocarbamoylmorpholine (6 g) (Nair 1966) and DMF acetal (12 ml) was heated at 100° for 6 hr. Excess DMF acetal was then removed *in vacuo*, the residue digested with hexane, cooled and filtered to give the formamidine derivative (7) (9 g), m.p. $84\text{--}86^\circ\text{C}$ (Found : C, 48.12 ; H, 7.64 ; N, 21.06. $\text{C}_8\text{H}_{15}\text{N}_3\text{OS}$ requires C, 47.75 ; H, 7.51 ; N, 20.88%). NMR (CDCl_3) : 3.05, 3.17 (2s, NMe_2) ; 3.5 to 4.5 (m, 8H) ; 8.72 (s, CH). MS : 201 (M^+).

The above formamidine derivative (7) (3 g) was refluxed with chloroacetone (1.5 g) in isopropanol (50 ml) for 3 hr and then the solvent stripped off. The residue was digested with water and extracted with ethyl acetate. Evaporation of the organic layer and crystallization of the residue from ethyl acetate-hexane gave 5-acetyl-2-morpholinothiazole (8) (2 g), m.p. $145\text{--}147^\circ\text{C}$ (Found : C, 51.24 ; H, 5.94 ; N, 13.54. $\text{C}_9\text{H}_{12}\text{N}_2\text{O}_2\text{S}$ requires C, 50.94 ; H, 5.70 ; N, 13.20%). NMR (CDCl_3) : 2.42 (s, Me) ; 3.5 to 4.0 (m, 8H) ; 7.72 (s, Ar-H). MS : 212 (M^+).

The formamidino thiourea (7) (1 g) was refluxed with phenacyl bromide (1 g) in isopropanol (20 ml) for 2 hr and then the solvent removed *in vacuo*. The residue was basified with NaHCO_3 solution and extracted with ethyl acetate. The ethyl acetate solution was concentrated to a small volume and treated with hexane to give 5-benzoyl-2-morpholinothiazole (9a) (1 g), m.p. $156\text{--}159^\circ\text{C}$ (Found : C, 61.49 ; H, 5.42 ; N, 9.91. $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$ requires C, 61.31 ; H, 5.15 ; N, 10.21%). NMR (CDCl_3) : 3.5 to 4 (m, 8H) ; 7.3 to 7.9 (m, 5 Ar-H) ; 7.67 (s, ArH). MS : 274 (M^+).

The formamidino thiourea (7) (5 g) was refluxed with 4-chloro-3-nitrophenacyl bromide (7 g) in isopropanol (100 ml) for $2\frac{1}{2}$ hr, cooled and the solid filtered. It was recrystallized first from ethyl acetate and then from chloroform-hexane to give 5-(4-chloro-3-nitro) benzoyl-2-morpholinothiazole (9b), (6 g), m.p. $203\text{--}205^\circ\text{C}$ (Found : C, 47.46 ; H, 3.69 ; N 11.50. $\text{C}_{14}\text{H}_{12}\text{ClN}_3\text{O}_4\text{S}$ requires C, 47.53 ; H, 3.42 ; N, 11.88%). NMR (DMSO-d_6) : 3.4 to 3.8 (m, 8H) ; 7.6 to 8.2 (4 Ar-H). MS : 353, 355 (M^+).

The formamidino thiourea (7) (3 g) was refluxed with ethyl chloroacetate (1.8 g) in isopropanol (50 ml) for 3 hr. After cooling, water (500 ml) was added, the solid filtered and recrystallized from ethyl acetate-hexane to give ethyl

2. Synthesis of 2-(N-methylpiperazino) thiazoles

A mixture of 1-thiocarbamoyl-4-methylpiperazine (Remers *et al* 1971) (12 g) and DMF acetal (18 g) was stirred and heated at 130° for 6 hr. The excess DMF acetal was then removed *in vacuo* and the residue digested with hexane, cooled and filtered to give the formamidine derivative (11), (11 g). A sample was recrystallized from methanol-ethyl acetate to give pure (11), m.p. 107–111° (Found: C, 46.74; H, 8.13; N, 23.73. $C_9H_{18}N_4S \cdot H_2O$ requires C, 46.53; H, 8.68; N, 24.12%). NMR ($CDCl_3$): 2.27 (s, NMe); 2.43 (t, $2CH_2$); 3.0 (s, NMe); 3.1 (s, NMe); 4.07 (t, CH_2); 4.30 (t, CH_2); 8.77 (s, CH). MS: 144 (M^+).

A similar reaction with DMA acetal gave the acetamidine derivative (12) as gum which was used as such for the subsequent reaction.

A mixture of the formamidinothiourea (11) (9.6 g) and *p*-nitrophenacyl bromide (11 g) in isopropanol (300 ml) was stirred and refluxed for 4 hr, then cooled and the solid filtered. This solid hydrobromide was basified with 2N NaOH, the liberated base extracted in methylene chloride, the solvent dried and evaporated. Recrystallization of the residue from ethyl acetate-methanol gave 2-(N-methyl piperazino)-5-(*p*-nitrobenzoyl) thiazole (13) (11 g), m.p. 187–190° C (Found: C, 53.92; H, 5.14; N, 16.74. $C_{15}H_{16}N_4O_3S$ requires C, 54.21; H, 4.85; N, 16.86%). MS: 332 (M^+).

A similar reaction of (11) (8.3 g) with *m*-nitrophenacyl bromide (9.5 g) in isopropanol gave 2-(N-methylpiperazino)-5-(*m*-nitrobenzoyl) thiazole (14) (6.7 g) which was crystallized from ethyl acetate, m.p. 153–157° C (Found: C, 54.08; H, 5.16; N, 16.97. $C_{15}H_{16}N_4O_3S$ requires C, 54.21; H, 4.85; N, 16.86%). MS: 332 (M^+).

Likewise, reaction of (11) (10.7 g) with 4-chloro-3-nitrophenacyl bromide (13.9 g) gave 5-(4-chloro-3-nitrobenzoyl)-2-(N-methylpiperazino) thiazole (15) (11 g), m.p. 156–160° C (from ethyl acetate-hexane) (Found: C, 49.21; H, 4.39; N, 14.97. $C_{15}H_{15}ClN_4O_3S$ requires C, 49.12; H, 4.12; N, 15.28%). NMR ($CDCl_3$): 2.27 (s, NMe); 2.47 (t, $2CH_2$); 3.70 (t, $2CH_2$); 7.5 to 8.3 (4Ar-H).

A mixture of the gummy acetamidino thiourea (12) (2.3 g) and *m*-nitrophenacyl bromide (2.4 g) was refluxed in isopropanol (50 ml) for 4 hr, cooled and filtered. The solid was basified with 2N NaOH and extracted with ethyl acetate. The organic layer was washed with water, dried and evaporated. Recrystallization of the residue from ethyl acetate-hexane gave 4-methyl-2-(N-methylpiperazino)-5-(*m*-nitrobenzoyl) thiazole (16) (1.2 g), m.p. 144–147° C. (Found: C, 55.48; H, 5.55; N, 16.39. $C_{16}H_{18}N_4O_3S$ requires C, 55.48; H, 5.24; N, 16.18%). NMR ($CDCl_3$): 2.27 (s, Me); 2.33 (s, NMe); 2.43 (t, $2CH_2$); 3.0 (t, $2CH_2$); 7.2 to 8.7 (4 Ar-H). MS: 346 (M^+).

Acknowledgements

We thank Dr S Selvavinayakam and his associates for the analytical and spectral

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Ried W and Kaiser L 1976 *Liebigs Ann. Chem.* 395

general synthesis of thiazoles. Part 6¹. Synthesis of amino-5-heterylthiazoles²

S RAJAPPA *, V SUDARSANAM** and V G YADAV

CIBA-GEIGY Research Centre, Goregaon, Bombay 400 063, India

**The Boots Company (India) Ltd., SION, Bombay 400 022, India

MS received 12 August 1982

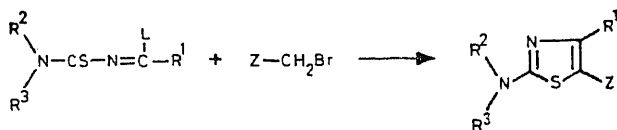
Abstract. 2-Chloromethyl pyridine, 2-chloromethyl quinoline and 2-chloromethyl benzimidazole have been reacted with amidino thioureas to provide the corresponding 2-amino-5-(2-heteroaryl) thiazoles. 4-Chloromethyl thiazole failed to undergo this reaction.

Keywords. 2-Amino-5-heteroarylthiazoles ; amidinothioureas.

Introduction

In the previous papers of this series, we have established the generality of the synthetic sequence shown in scheme 1 for preparing a variety of thiazoles. In this sequence, L is a suitable leaving group (NR_2 or OR), and Z is a group that activates the adjacent methylene for cyclization. Normally such activation is provided by a carbonyl; we have also recorded examples where Z is NO_2 (Rajappa and Sreenivasan 1978). In this paper we have enlarged the scope of the synthesis by proving that Z can also be a suitable heteroaryl radical.

Scheme 1



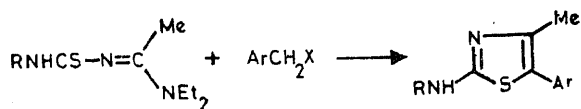
To whom correspondence should be made.

Part 5. Preceding paper.

Contribution No. 675 from CIBA-GEIGY Research Centre

The adduct (1) of methyl isothiocyanate and N,N-diethyl-acetamidine was chosen as the first substrate to be reacted with chloromethyl heterocycles. The feasibility of providing sufficient activation for the methylene group by means of an adjacent suitably substituted aryl group was first proved by condensation of (1) with *p*-nitrobenzyl bromide. This led to the formation of 5-*p*-nitrophenylthiazole (4). A similar reaction has been described by Ried and Kaiser (1976). The stage was now set for investigating halomethyl heterocycles as reactants in this synthesis. We were pleased to find that 2-chloromethylpyridine and 2-chloromethylquinoline gave (5) and (6) respectively in a clean reaction with (1). Likewise, 2-chloromethyl-benzimidazole also participated in the reaction, leading to the 2-benzimidazolyl derivative (7). However, 4-chloromethylthiazole did not possess a methylene group reactive enough to take part in the cyclization.

The 2-anilino-5-(2-pyridyl) thiazole (8) was similarly prepared from the phenyl isothiocyanate-N,N-diethyl-acetamidine adduct (2) and 2-chloromethylpyridine. 5-Heteryl thiazole-2-carbamates can be synthesised with equal facility by this procedure. Thus the 5-(2-benzimidazolyl) thiazole-2-carbamates



(1) R = Me

(2) R = Ph

(3) R = CO₂Et

(4) R = Me, Ar = 4-NO₂-C₆H₄

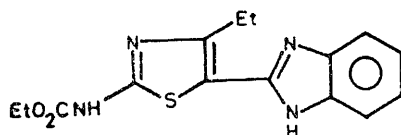
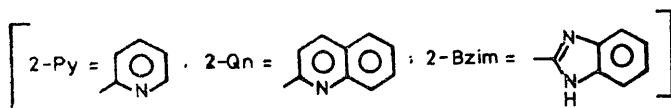
(5) R = Me, Ar = 2-Py

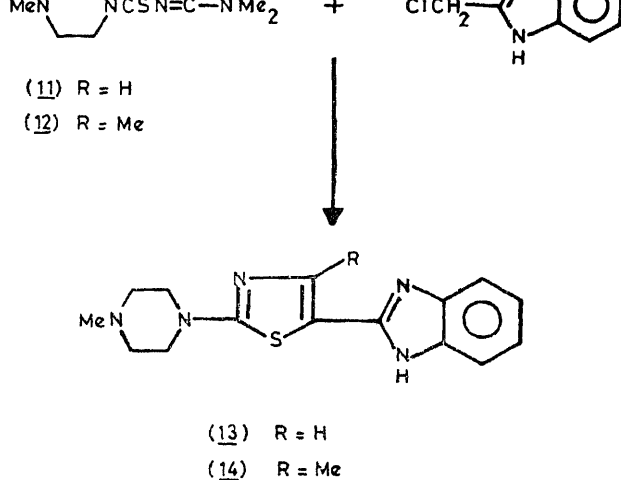
(6) R = Me, Ar = 2-Qn

(7) R = Me, Ar = 2-Bzim

(8) R = Ph, Ar = 2-Py

(9) R = CO₂Et, Ar = 2-Bzim





(9) and (10) were obtained from the adducts of carbethoxyisothiocyanate with N,N-diethylacetamidine and N,N-diethylpropionamidine respectively.

The methodology for preparing 2-dialkylaminothiazoles was discussed in the previous paper of this series. The same starting materials (11) and (12) were also useful in synthesising the 5-(2-benzimidazolyl)-2-(N-methylpiperazino) thiazoles (13) and (14) respectively; however, the yields were low in this reaction, probably due to the quaternization of the piperazine nitrogen.

Experimental

Melting points are uncorrected. ^1H NMR spectra were recorded either on a Varian A 60 or a Varian EM 360 L spectrometer. Chemical shifts are expressed in δ values (ppm) downfield from TMS. Mass spectra were determined on a Varian Mat CH 7 instrument at 70 eV utilizing direct insertion.

1. 5-Aryl-4-methyl-2-methylaminothiazoles

A mixture of methyl isothiocyanate (20 g) and N,N-diethylacetamidine (31 g) was left at 30° overnight, then digested with ether, cooled and filtered to get the adduct (1) (36.1 g, m.p. 69–72° C).

The adduct (1) (3 g) and *p*-nitrobenzyl bromide (3.5 g) were refluxed in isopropanol (25 ml) for 6 hr, cooled and filtered. The solid was taken in cold water, basified with KHCO_3 and filtered. Recrystallization of the solid from isopropanol gave 4-methyl-2-methylamino-5-(*p*-nitrophenyl) thiazole (4) (3 g, m.p. 13–205° C (Found : C, 53.30; H, 4.80; N, 16.53. $\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}_2\text{S}$ requires C, 53.01; H, 4.45; N, 16.86%). NMR ($\text{DMSO}-d_6$): 2.33 (s, Me); 2.87 (s, Me); 7.5 (d, 2 Ar-H); 7.83 (q, NH); 8.17 (d, 2Ar-H). MS : 249 (M⁺).

The adduct (1) (3 g) was refluxed in isopropanol (25 ml) for 6 hr with 2-chloromethylpyridine (liberated from 2.5 g of the hydrochloride). The solvent was then removed *in vacuo*, the residue dissolved in cold water, basified with KHCO_3 solution and the solid filtered. Recrystallization from ethanol gave 4-methyl-2-methylamino-5-(2-pyridyl) thiazole (5) (2.3 g), m.p. 188–191° C. (Found : C, 58.48 ; H, 5.68 ; N, 20.75. $\text{C}_{10}\text{H}_{11}\text{N}_3\text{S}$ requires C, 58.53 ; H, 5.40 ; N, 20.48%). NMR (DMSO-d_6): 2.43 (s, Me) ; 2.87 (br, s, Me) ; 6.9 to 8.6 (4 Ar-H). MS : 205 (M^+).

A similar reaction of (1) (3 g) with 2-chloromethyl quinoline (liberated from 3.6 g of the hydrochloride) gave, after crystallization from ethanol, 4-methyl-2-methylamino-5-(2-quinolyl) thiazole (6) (2.3 g), m.p. 203–205° (Found : C, 65.58 ; H, 5.25 ; N, 16.43. $\text{C}_{14}\text{H}_{13}\text{N}_3\text{S}$ requires C, 65.87 ; H, 5.13 ; N, 16.46%). NMR (DMSO-d_6): 2.43 (s, Me) ; 2.9 (dr, s, Me) ; 7.2 to 8.4 (6 Ar-H). MS : 255 (M^+).

The adduct (1) (3 g) and 2-chloromethylbenzimidazole (3 g) were refluxed in isopropanol (50 ml) for 6 hr, cooled and filtered. Conversion of the solid hydrochloride into the free base and crystallization from methanol-ethanol gave 5-(2-benzimidazolyl)-4-methyl-2-methylaminothiazole (7) (0.8 g), m.p. 315–320° C. More of the same substance was obtained from the isopropanol filtrate by evaporation and basification (Found : C, 59.13 ; H, 5.26 ; N, 23.25. $\text{C}_{12}\text{H}_{12}\text{N}_4\text{S}$ requires C, 59.01 ; H, 4.95 ; N, 22.94%). NMR (DMSO-d_6) : 2.57 (s, Me) ; 2.83 (d, Me) ; 6.9 to 7.6 (m, 4 Ar-H) ; 7.83 (q, NH). MS : 244 (M^+).

3.2. 2-Anilino-4-methyl-5-(2-pyridyl) thiazole

Phenyl isothiocyanate (13.5 g) and N,N -diethylacetamide (10.2 g) were mixed and stirred at 0° in isopropanol for $2\frac{1}{2}$ hr, and left at 30° overnight. The solid was filtered and recrystallized from methylene chloride-ether to give the adduct (2) (19.3 g), m.p. 132° C (Found : C, 62.31 ; H, 7.66 ; N, 17.07. $\text{C}_{13}\text{H}_{13}\text{N}_3\text{S}$ requires C, 62.62 ; H, 7.68 ; N, 16.86%). NMR (CDCl_3) : 1.17 (t, 2Me) ; 2.5 (s, Me) ; 3.4 (q, 2CH_2) ; 6.9 to 7.5 (5 Ar-H) ; 8.9 (NH).

The above adduct (2) (2 g) was refluxed in isopropanol (25 ml) with 2-chloromethylpyridine (liberated from 1.3 g of the hydrochloride) for 6 hr. The solvent was then removed *in vacuo*, the residue dissolved in cold water, basified with KHCO_3 solution and extracted with ethyl acetate. The organic layer was dried and concentrated. Addition of ether to this gave 2-anilino-4-methyl-5-(2-pyridyl) thiazole (8) (0.85 g), m.p. 153° C (Found : C, 67.25 ; H, 5.01 ; N, 15.42. $\text{C}_{15}\text{H}_{13}\text{N}_3\text{S}$ requires C, 67.40 ; H, 4.90 ; N, 15.72%). NMR (CDCl_3) : 2.5 (s, Me) ; 6.8 to 8.6 (9 Ar-H and 1 NH). MS : 267 (M^+).

anol to give 5-(2-benzimidazolyl)-4-methylthiazole-2-carbamic acid ethyl ester (4.5 g), m.p. 260–261° C (Found : C, 55.60 ; H, 4.90 ; N, 18.62. $\text{C}_{14}\text{H}_{14}\text{N}_4\text{O}_2\text{S}$ requires C, 55.62 ; H, 4.67 ; N, 18.54%). NMR (DMSO-d_6) : 1.2 (Me) ; 1.5 (s, Me) ; 4.05 (q, CH_2) ; 6.9 to 7.6 (4 Ar-H).

A similar addition of carbethoxy isothiocyanate (10 g) to N,N-diethyl-pionamidine (10 g) followed by reaction with 2-chloromethyl benzimidazole (g) in ethanol (400 ml) gave 5-(2-benzimidazolyl)-4-ethylthiazole-2-carbamic acid ethyl ester (10), (11.5 g), m.p. 237° C (Found : C, 57.02 ; H, 5.39 ; N, 18.08. $\text{C}_{15}\text{H}_{16}\text{N}_4\text{O}_2\text{S}$ requires C, 56.96 ; H, 5.10 ; N, 17.71%). NMR (DMSO-d_6) : 1.33 (t, 2Me) ; 3.2 (q, CH_2) ; 4.33 (q, CH_2) ; 7.1 to 7.8 (Ar-H). MS : 316 (M^+).

5-(2-Benzimidazolyl)-2-(N-methylpiperazino) thiazoles

The formamidinothiourea (11) (Rajappa *et al* 1982) (10.4 g) was stirred and refluxed in isopropanol (500 ml) with 2-chloromethyl benzimidazole (8.2 g) for 4 hr. The solvent was removed *in vacuo*, the residue dissolved in water, basified and extracted with methylene chloride. After drying, the solvent was evaporated and the residue crystallized from ethanol to give 5-(2-benzimidazolyl)-2-(N-methylpiperazino) thiazole (13) (0.8 g), m.p. 255–258° C. (Found : C, 60.49 ; H, 5.97 ; N, 23.05. $\text{C}_{15}\text{H}_{17}\text{N}_5\text{S}$ requires C, 60.19 ; H, 5.72 ; N, 23.40%). NMR (DMSO-d_6) : 2.27 (s, Me) ; 2.53 (m, 4H) ; 3.5 (m, 4H) ; 7.0 to 7.7 (4 Ar-H) ; 7.9 (s, Ar-H). MS : 299 (M^+).

Similar reaction of the acetamidino thiourea (12) (12 g) with 2-chloromethyl benzimidazole (8.5 g) gave 5-(2-benzimidazolyl)-4-methyl-2-(N-methylpiperazino) thiazole (14) (1.2 g), m.p. 257–260° C (Found : C, 61.65 ; H, 6.40 ; N, 22.46. $\text{C}_{15}\text{H}_{19}\text{N}_5\text{S}$ requires C, 61.32 ; H, 6.11 ; N, 22.35%). NMR (DMSO-d_6) : 2.23 (Me) ; 2.47 (m, 4H) ; 2.57 (s, ME) ; 3.4 (m, 4H) ; 7.0 to 7.7 (m, 4 Ar-H) ; 7.0 (NH). MS : 313 (M^+).

Acknowledgement

We thank Dr S Selvavinayakam and his associates for the analytical and spectral data.

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general synthesis of thiazoles. Part 7¹. Direct generation of chloromethyl 5-thiazolyl ketones²

S RAJAPPA*, V SUDARSANAM** and R SREENIVASAN

CIBA-GEIGY Research Centre, Goregaon, Bombay 400 063, India

**The Boots Company (India) Ltd., Sion, Bombay 400 022, India

MS received 12 August 1982

Abstract. Careful reaction of equimolar amounts of 1, 3-dichloroacetone and the amidinothiouras (4), (5), (6) or (10) has given the (2-amino-5-thiazolyl) chloromethyl ketones (7), (8), (9) and (11) respectively in 20 to 40% yields. The presence of excess amidinothiourea in the reaction mixture leads to the bis thiazolyl ketones (3).

Keywords. (2-amino-5-thiazolyl) chloromethyl ketones; direct synthesis; dichloroacetone; amidinothiouras.

Introduction

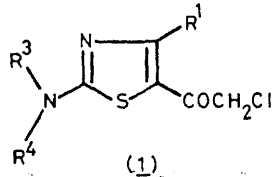
As part of a project on the synthesis of thiazole analogs of the known anthelmintic, Levamisole (Janssen 1976) we needed chloromethyl 5-thiazolyl ketones of the general structure (1). The disposition of the substituents in (1) was such that it was tempting to apply the general synthetic route developed by us to arrive at this structure directly. One specifically notes the presence of a 2-amino substituent and the carbonyl group attached to position 5 of the thiazole—features which are ideally generated by the novel sequence developed by us (Rajappa and Advani 1970). It is also to be noted that the normal procedure for getting such “phenacyl halides” would be the halogenation of an appropriate methyl ketone—a process which is not likely to yield the required product (1) cleanly when amine substituents are present.

The general synthesis of thiazoles can be represented as shown in scheme 1; compound (2) is a functionalised thiourea derivative in which L is a leaving group (R₂ or OR). The application of this reaction to prepare compounds of the type (1) would entail the use of 1,3-dichloroacetone as the carbonyl component (L = ClCH₂-). We recognized that the danger lay in the further condensation

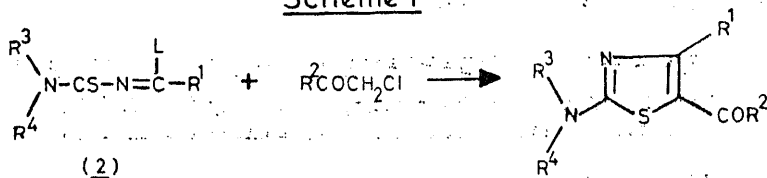
To whom correspondence should be made.

Part 6. Preceding paper.

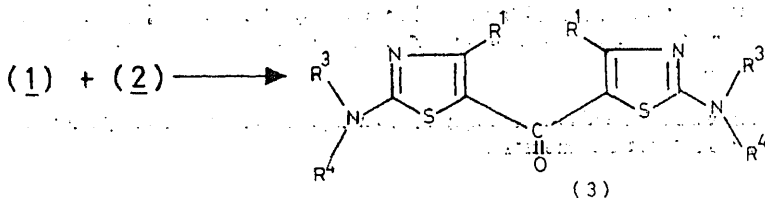
Contribution No. 676 from CIBA-GEIGY Research Centre.



Scheme 1



Scheme 2



of the product (1) with a second molecule of (2) to form the bis-thiazolyl ketone (3) (scheme 2).

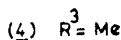
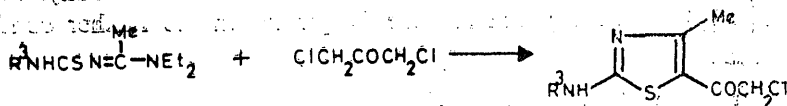
As described in our earlier papers, the nature of the substituents R^1 , R^3 and R^4 in compound (1) dictate the choice of the starting material (2) for the thiazole synthesis. We have used thiourea derivatives obtained by three different routes in our present investigations.

2. Results and discussion

2.1. Amidine-isothiocyanate adducts (scheme 3)

N,N-Diethyl acetamidine was added to methyl and *n*-butyl isothiocyanates to give the adducts (4) and (5). When equimolar amounts of (4) and 1, 3-dichloro-

Scheme 3



ld. The adduct (5) similarly gave (8) in 35% yield. As expected, the use of two moles of the thiourea component (4) to one of dichloroacetone gave the bisthiazolyl ketone (3) ($R^1 = R^3 = \text{Me}$; $R^4 = \text{H}$). The adduct (6) of carbonyl-isothiocyanate and N,N-diethylacetamidine gave both the monomer (9) and dimer (3) ($R^1 = \text{Me}$; $R^3 = \text{CO}_2\text{Et}$; $R^4 = \text{H}$) with one mole of dichloroacetone.

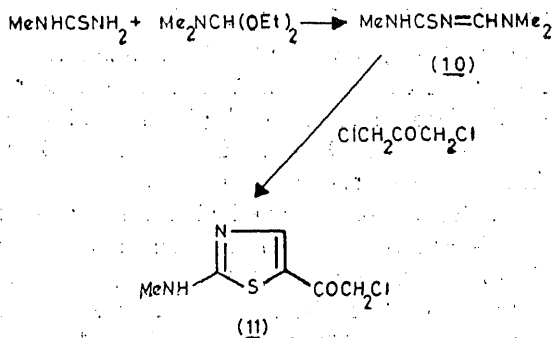
2. Thiourea-DMF acetal condensation product (scheme 4)

The formamidinothiourea (10) could be obtained from N-methylthiourea and DMF acetal. This reacted with 1,3-dichloroacetone to give the thiazole (11) in 35% yield.

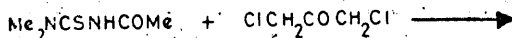
3. Acylthiourea

When the acylthiourea (12) was treated with an equimolar quantity of 1,3-dichloroacetone, only the bis thiazolyl ketone (3) ($R^1 = R^3 = R^4 = \text{Me}$) was obtained (scheme 5). We therefore abandoned any further attempt to generate chloromethyl 5-thiazolyl ketone of type (1) from acylthioureas.

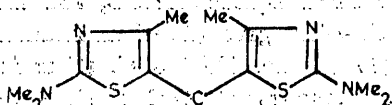
Scheme 4



Scheme 5



(12)



Melting points are uncorrected. ^1H NMR spectra were recorded on a Varian EM 360L spectrometer. Chemical shifts are expressed in δ values (ppm) downfield from TMS. Mass spectra were taken on a Varian Mat CH 7 instrument at 70 eV utilizing direct insertion.

3.1. Reaction of amidine-isothiocyanate adducts with 1, 3-dichloroacetone

The adduct (4) (5.6 g) (Rajappa *et al* 1982) was dissolved in isopropanol (50 ml) and added dropwise with stirring to a solution of 1, 3-dichloroacetone (3.8 g) in isopropanol (50 ml). The mixture was stirred and refluxed for 2 hr, cooled and the solvent evaporated *in vacuo*. The residue was treated with isopropyl HCl and again evaporated. Addition of isopropanol and ether gave a solid, which was filtered and recrystallized from methanol-isopropanol to yield chloromethyl [(4-methyl-2-methylamino)-5-thiazolyl] ketone hydrochloride (7) (1.5 g), m.p. 225–228° C (d). (Found : C, 35.04 ; H, 4.19 ; N, 11.96. $\text{C}_7\text{H}_9\text{ClN}_2\text{OS} \cdot \text{HCl}$ requires C, 34.87 ; H, 4.18 ; N, 11.62%). NMR ($\text{DMSO}-d_6$) : 2.2 (s, Me) ; 2.63 (s, Me) ; 4.5 (s, CH_2).

Reaction of 1, 3-dichloroacetone (1.27 g ; 0.01 mole) with the adduct (4) (3.74 g ; 0.02 mole) in refluxing isopropanol for 2 hr gave bis (4-methyl-2-methylamino-5-thiazolyl) ketone (0.5 g), which was recrystallized from aqueous acetic acid ; m.p. 290–295° (d). (Found : C, 46.94 ; H, 5.33 ; N, 20.16. $\text{C}_{11}\text{H}_{14}\text{N}_4\text{OS}_2$ requires C, 46.81 ; H, 5.00 ; N, 19.85%). MS : 282 (M^+).

n-Butyl isothiocyanate (3.5 g) was mixed with N,N-diethylacetamidine (3.5 g) ; the mixture was maintained at 100° C for 2 hr and then cooled. The adduct (5) thus obtained was dissolved in isopropanol (50 ml) and added dropwise with stirring to 1, 3-dichloroacetone (3.9 g) in isopropanol (50 ml). The mixture was stirred and refluxed for 3 hr, evaporated and the product converted as before to the hydrochloride. This was recrystallized from methanol-isopropanol to give (2-*n*-butylamino-4-methyl-5-thiazolyl) chloromethyl ketone hydrochloride (8) (3 g), m.p. 185–190° C (d). (Found : C, 43.16 ; H, 6.13 ; N, 10.26. $\text{C}_{10}\text{H}_{18}\text{ClN}_2\text{OS} \cdot \text{HCl}$ requires C, 42.41 ; H, 5.69 ; N, 9.89%). NMR (TFA) : 1.07 (t, Me) ; 1.7 (m, 4H) ; 2.8 (s, Me) ; 3.57 (q, CH_2), 4.6 (s, CH_2).

Carbethoxy isothiocyanate (32.7g) was added dropwise at 0–5° to N,N-diethylacetamidine (28.5 g) and then stirred at 5° for 2 hr. The adduct thus formed was dissolved in isopropanol (200 ml), added to 1, 3-dichloroacetone (31.8 g) in isopropanol (200 ml) and refluxed for 5 hr. After cooling the solid was filtered, converted to the base with saturated aqueous KHCO_3 and filtered to give the dimer, bis (2-carbethoxyamino-4-methyl-5-thiazolyl) ketone, (15 g), m.p. 328° C. (Found : C, 45.59 ; H, 4.91 ; N, 13.85. $\text{C}_{15}\text{H}_{18}\text{N}_4\text{O}_6\text{S}_2$ requires C, 45.23 ; H, 4.55 ; N, 14.07%). The isopropanol filtrate was evaporated *in vacuo*, basified with saturated aqueous KHCO_3 and filtered. Recrystallization of this solid from CH_2Cl_2 -ether gave (2-carbethoxyamino-4-methyl-5-thiazolyl) chloromethyl ketone (9) (17 g), m.p. 135–138° C. (Found : C, 41.44 ; H, 4.49 ; N, 11.03. $\text{C}_7\text{H}_9\text{ClN}_2\text{OS}$ requires C, 41.15 ; H, 4.22 ; N, 10.78%).

CDCl_3); 1.4 (t, Me); 2.75 (s, Me); 4.42 (q, CH_2); 4.5 (s, CH_2). MS: m/z 264 (M^+).

2. Reaction of the formamidinothiourea (10) with 1,3-dichloroacetone

A mixture of N-methylthiourea (60 g), DMF acetal (80 g) and *p*-toluene sulfonic acid (2 g) in benzene (500 ml) was refluxed in an apparatus attached to a Dean-Stark water-separator for 5 hr. The solution was then concentrated, treated with hexane, cooled and filtered to give (10) (75 g), m.p. 108–112°. (Found C, 41.56; H, 7.68; N, 29.10. $\text{C}_5\text{H}_{11}\text{N}_3\text{S}$ requires C, 41.37; H, 7.64; N, 28.95%).

A mixture of the formamidinothiourea (10) (4.3 g) and 1, 3-dichloroacetone (7 g) was refluxed in isopropanol (100 ml) for 3 hr and the solvent then removed *in vacuo*. The residue was digested with water, filtered and recrystallized from methanol-ethyl acetate to give chloromethyl [(2-methylamino)-5-thiazolyl] ketone (11) (2.3 g), m.p. 162–166° C (d). Found: C, 38.16; H, 13; N, 14.89. $\text{C}_6\text{H}_7\text{ClN}_2\text{OS}$ requires C, 37.80; H, 3.70; N, 14.70%. IR ($\text{CDCl}_3 + \text{DMSO-d}_6$): 2.97 (s, Me); 4.63 (s, CH_2); 8.05 (s, Ar-H).

3. Reaction of the acylthiourea (12) with 1,3-dichloroacetone

N-Acetylthiourea (12) (4.4 g) (Sandström 1963) was dissolved in isopropanol (100 ml) and added dropwise with stirring to a solution of 1, 3-dichloroacetone (8 g) in isopropanol (50 ml). The mixture was refluxed for 3 hr, concentrated and cooled. The solid was filtered and recrystallized from isopropanol to give the hydrochloride of bis (2-dimethylamino-4-methyl-5-thiazolyl) ketone (5 g), m.p. 228–233° C (d). NMR (D_2O): 2.13 (s, Me); 3.0 (s, NMe_2).

The free base was liberated from this by means of NaHCO_3 and recrystallized from ethyl acetate-hexane; m.p. 149–151° C. (Found: C, 50.60; H, 6.16; N, 18.39. $\text{C}_{13}\text{H}_{18}\text{N}_4\text{OS}_2$ requires C, 50.31; H, 5.85; N, 18.06%). MS: 310 (M^+),

Acknowledgement

We thank Dr S Selvavinayakam and his associates for the analytical and spectral data.

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Nitroenamines. Part 9¹. The enaminic reactivity of nitromethylenethiazolidine²

S RAJAPPA* and B G ADVANI

CIBA-GEIGY Research Centre, Goregaon, Bombay 400 063, India

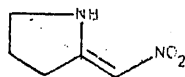
MS received 12 August 1982

Abstract. 2-Nitromethylenethiazolidine has been synthesised and found to be a weak enamine. It reacts with acyl isothiocyanates but not with phenyl isothiocyanate. Oxidative cyclization of the acyl isothiocyanate adducts leads to isothiazolo [3,2-b] thiazole derivatives. The 2-benzoylimino compound 8 undergoes base catalysed fragmentation to give the nitronitrile 9.

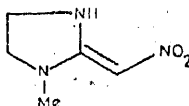
Keywords. Nitroenamine; enaminic reactivity; cyanolation; push-pull ethylene.

Introduction

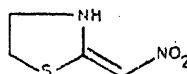
In the past, we have compared the nucleophilic reactivity of cyclic nitrovinylamines such as 1 and nitroketeneaminals such as 2 (Rajappa 1981). The latter were found to be more reactive than the former towards electrophiles. We wanted to extend our investigation to 2-nitromethylenethiazolidine 3 to find out if the sulfur lone-pairs would effectively conjugate with the nitrovinyl system.



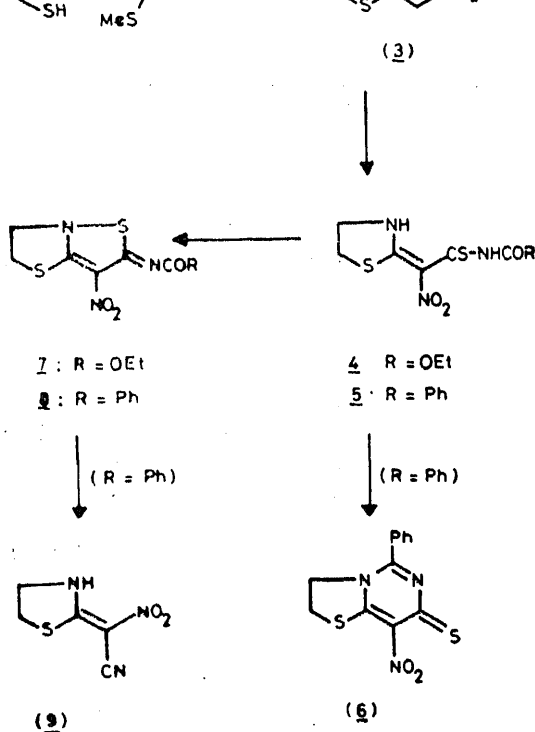
(1)



(2)



(3)



2. Results and discussion

2-Nitromethylenethiazolidine (3) has been synthesised earlier from 2-methylthiazoline by nitration with *n*-propyl nitrate in liquid ammonia in presence of sodium amide (Feuer and Lawrence 1972). We have now prepared the compound by the action of cysteamine on 1,1-bis (methyl-mercapto)-2-nitroethylene (scheme 1).

We had earlier concluded that isothiocyanates constituted ideal probes to delineate the enaminic reactivity of nitroenamines. Accordingly, we set out to map the reactivity of 3 towards various isothiocyanates. The compound was recovered unreacted after refluxing for 16 hr with phenyl isothiocyanate in acetonitrile solution. However, the more reactive acyl isothiocyanates formed adducts with 3. Thus carbethoxy isothiocyanate gave the adduct 4, while benzoyl isothiocyanate gave 5. Although these adducts could not be obtained in crystalline form, their subsequent reactions left no doubt as to their identity. It turns out thus that in its enaminic reactivity, 2-nitromethylene thiazolidine 3 resembles the nitrovinylamine 1 rather than the nitroketeneaminal 2.

Acyl isothiocyanate adducts of nitroenamines have served as useful starting materials for other types of nitro derivatives (Rajappa 1977). We have subjected

phenyl-6,7-dihydro-3H-thiazolo [3,2-c] pyrimidine-3-thione (6); in fact, this conversion takes place even during the work-up of (5). Both (4) and (5) could be oxidized by bromine to produce the 2-acylimino-3-nitro-5,6-dihydro-2H-isothiazolo [3,2-b] thiazoles (7) and (8) respectively; in this reaction, a bond is created between the ring nitrogen and the sulfur atom of the thiocarbonyl group.

A reaction of special significance to nitroenamine chemistry is the base-catalysed fragmentation of 5-benzoylimino-4-nitroisothiazolines with extrusion of sulfur (Rajappa *et al* 1977). The presence of this moiety in (8) prompted us to examine its behaviour towards sodium ethoxide. It was gratifying to find that the isothiazolo [3,2-b] thiazole (8) also undergoes this characteristic fragmentation reaction, leading to 2-(α -cyano- α -nitro) methylenethiazolidine (9) in 19% yield. The net result of the three step sequence comprising of adduct formation (5), oxidative cyclization (8) and fragmentation is thus the "cyanolation" of 2-nitromethylene-thiazolidine; This is equivalent to reaction of enamine with CN^+ . The product (9) is a novel push-pull ethylene.

3. Experimental

Melting points are uncorrected. Mass spectra were recorded on a Varian Mat CH 7 instrument at 70 eV utilizing direct insertion.

3.1. Synthesis of 2-nitromethylene thiazolidine (3)

A suspension of 1,1-bis (methylmercapto)-2-nitroethylene (16 g) in ethanol (180 ml) was stirred under nitrogen with cysteamine (10 g) for 18 hr at 30°C and then left for 2 days. The solid was filtered and extracted with boiling isopropanol. The insoluble residue was discarded. The product (3) crystallized from isopropanol; yield 6 g, m.p. 141–143°C (Found: C, 32.85; H, 4.28; N, 18.90. $\text{C}_4\text{H}_6\text{N}_2\text{O}_2\text{S}_2$ requires C, 32.88; H, 4.14; N, 19.18%). MS: 146 (M⁺).

3.2. Reaction of (3) with acyl isothiocyanates

3.2a. *With carbethoxy isothiocyanate*: A solution of 3 (1.5 g) in acetonitrille (25 ml) was treated with carbethoxy isothiocyanate (1.3 g) at 30° and left for 3 hr. The solvent was removed *in vacuo* and the residue dissolved in ethyl acetate. The small amount of insoluble material was discarded and the solution containing (4) used as such for the oxidative cyclization (see below).

3.2b. *With benzoyl isothiocyanate*: A solution of 3 (4.5 g) in acetonitrile (75 ml) was treated with benzoyl isothiocyanate (4.8 g) at 30°, and left for 16 hr. The solvent was removed *in vacuo*, the residue digested with chloroform and filtered. The filtrate containing the adduct (5) was used as such for the oxidative cyclization (see below). The chloroform-insoluble solid was recrystallized from methylene chloride-hexane to give 6, (3 g), m.p. 193–194° (Found: C, 49.70; H, 3.22; N, 14.09. $\text{C}_{15}\text{H}_9\text{N}_3\text{O}_2\text{S}_2$ requires C, 49.47; H, 3.12; N, 14.43%).

3.3. Oxidative cyclization of the adducts 4 and 5

The ethyl acetate solution containing the adduct 4 was cooled to 10° and treated dropwise with stirring with bromine (1.4 g) in ethyl acetate (10 ml). After the addition was over, ether was added and the precipitated solid filtered. This was basified with NaHCO₃ and the base recrystallized from acetonitrile to give the isothiazolo [3,2-b] thiazole 7 (0.9 g), m.p. 220–221°C (Found : C, 35.31 ; H, 3.46 ; N, 15.25. C₈H₉N₃O₄S₂ requires C, 34.92 ; H, 3.30 ; N, 15.27%). MS : 275 (M⁺).

The chloroform solution containing the adduct 5 was similarly oxidized with bromine (3.5 g) in chloroform (15 ml). Saturated NaHCO₃ solution (100 ml) was added after 15 min, stirred for 30 min, and the solid filtered. Trituration with ethanol gave the isothiazolo, [3,2-b] thiazole 8 (2.0 g), m.p. 250–255°. A sample was recrystallized from acetic acid to give the pure 8, m.p. 265–268° (Found : C, 46.86 ; H, 3.16 ; N, 13.48. C₁₂H₉N₃O₃S₂ requires C, 46.91 ; H, 2.95 ; N, 13.68%). MS : 307 (M⁺).

3.4. 2-(α -cyano- α -nitro) methylene thiazolidine (9)

Sodium ethoxide was prepared by dissolving sodium metal (0.3 g) in absolute ethanol (50 ml). To this solution was added 2-benzoylimino-3-nitro-5,6-dihydro-2H-isothiazolo [3,2-b] thiazole (8) (2.8 g), and the mixture refluxed with stirring for 2 hr. The solvent was then removed *in vacuo*, and the residue dissolved in water and filtered. The filtrate was extracted with ether to remove ethyl benzoate. The aqueous solution was cooled and acidified with acetic acid. The solid, that separated, was filtered and recrystallized from acetonitrile-methanol to give the nitronitrile 9 (0.3 g), m.p. 227–230°C (d), after becoming black at 200°C (Found : C, 34.95 ; H, 3.35 ; N, 24.38. C₅H₅N₃O₂S requires C, 35.09 ; H, 2.95 ; N, 24.56%). IR (nujol) : 2220 cm⁻¹ (CN). MS : 171 (M⁺).

Acknowledgement

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Tl(III) acetate oxidation of cyclanols and bicyclo(2,2,1) heptan-2-ols

VANGALUR S SRINIVASAN* and N VENKATASUBRAMANIAN†

Department of Chemistry, Vivekananda College, Mylapore, Madras 600 004, India

† IDL—Nitro Nobel Basic Research Institute, P.B. No. 397, Bangalore 560 003, India

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Abstract. Tl(III) acetate oxidation of cyclohexanol, cyclopentanol, cycloheptanol, *trans*-2-chlorocyclohexanol, *cis*-4-*t*-butylcyclohexanol, *trans*-4-*t*-butylcyclohexanol, borneol, isoborneol, *exo* (β) norborneol and *endo* (α) norborneol has been studied in the presence of 0.90 M H_2SO_4 . The observed reactivity pattern among the cyclanols is cyclopentanol < cyclohexanol > cycloheptanol < cyclooctanol which is the same as the one noted in V(V) oxidation of the substrates under similar conditions—an order contrary to the I-strain concept. In both cases Mn(II) catalysis and acrylonitrile polymerisation have been observed in cyclohexanol oxidation alone. The kinetic isotope effect in the Tl(III) oxidation of cyclohexanol is 2.82 as against a value of 6.4 obtained for Tl(III) oxidation of benzhydrol. The kinetic observations are explained on the basis of a radical mechanism operating in the case of cyclohexanol, as it is a strainless ring system, with the intermediacy of Tl(II). *Trans*-2-chloro and *trans*-2-phenyl groups, due-I effect, retard the rate of the reaction. *Cis*-4-*t*-butylcyclohexanol reacts faster than the *trans* compound due to relief of strain in the transition state. The reactivity pattern among the bicyclo (2,2,1) heptan-2-ols is, isoborneol > borneol > *exo* (β)-norborneol > cyclopentanol > *endo*-(α)-norborneol. This is consistent with the relief of strain in the transition state due to the hybridisation change from sp^3 to sp^2 and lessening of torsional interaction. This can also be due to the formation of less-strained products.

Keywords. Tl(III) acetate oxidation ; stereochemical aspects.

1. Introduction

The survey of literature indicates that the kinetic and mechanistic aspects of oxidation of alicyclic alcohol by Tl(III) has not been studied so far. The present work on Tl(III) oxidation of cyclopentanol, cyclohexanol, cycloheptanol, cyclooctanol, *trans*-2-chlorocyclohexanol, *trans*-2-phenylcyclohexanol, *trans*-4-*t*-butylcyclohexanol and *cis*-4-*t*-butylcyclohexanol, throws light on the effect of ring size on the oxidation rate and stereochemical and electronic effects on these reactions.

* To whom all correspondence should be made.

2. Results and discussion

The oxidations were carried out in 50% HOAc-50% H₂O mixture in the presence of 0.9 M H₂SO₄. The individual rate behaviour with reference to cyclohexanol, cyclopentanol, cyclooctanol, *trans*-2-chlorocyclohexanol and borneol was investigated (table 1). The reaction exhibits total second order kinetics—first order with respect to each reactant. The rate law is, therefore,

$$-\frac{d[\text{Ti(III)}]}{dt} = k_2 [\text{Ti(III)}] [\text{alcohol}]$$

2.1. Dependence of rate on sulphuric acid concentration

With increasing concentration of sulphuric acid, the rate of oxidation increases in the range 0.9M—3.0M (table 2). This shows that this reaction is an acid catalysed one.

2.2. Effect of added Mn(II)

While the addition of Mn(II) has negligible influence in the Ti(III) oxidation of α -phenyl ethyl alcohol and cyclopentanol, it is interesting to note, that only in the case of cyclohexanol oxidation, there is a pronounced increase in rate with increasing Mn(II) concentration (table 3). Also this reaction alone initiates acrylonitrile polymerisation. The above facts point to a different type of mechanism operating in the Ti(III) oxidation of cyclohexanol.

2.3. Ring size and reactivity

A perusal of data in table 4 shows the following order of reactivity among cyclanols : cyclopentanol < cyclohexanol > cycloheptanol < cyclooctanol. This result is surprising and unexpected in alicyclic system, which is governed by the I-strain (Gerstein and Brown 1950 ; Fletcher *et al* 1951 ; Brown 1956). One would have expected the following order of reactivity, cyclopentanol > cyclohexanol < cycloheptanol < cyclooctanol as was in the Cr(VI) oxidation of these substrates (Srinivasan and Venkatasubramanian 1967 ; Richer and Hoa 1969). Similar results contrary to I-strain concept is obtained in the V(V) oxidation of cyclanols where the same order of reactivity has been observed (Ganapathisundaram 1970). A plot of $\log k_{2\text{ V(V)}}$ versus $\log k_{2\text{ Ti(III)}}$ is linear indicating similar transition state in both the cases. It is pertinent to point out here that in the V(V) oxidation of cyclohexanol, Mn(II) catalysis was observed and the reaction also induced acrylonitrile polymerisation. The results contrary to I-strain concept in Ti(III) oxidation of cyclanols is therefore, due to a different type of mechanism operating in this case. The mechanism of V(V) oxidation of cyclohexanol involves the formation of a radical formed by the homolytic cleavage of C-H bond (Littler and Waters 1959). Probably in the Ti(III) oxidation of cyclohexanol,

The rates of oxidation of *trans*-2-chlorocyclohexanol and *trans*-2-phenylcyclohexanol are considerably slower than cyclohexanol which can be attributed to -I effect of the 2-chloro and 2-phenyl groups. The stereoisomeric substrates like *cis*- and *trans*-4-*t*-butylcyclohexanols are oxidised by Tl(III)—the *cis* compound getting oxidised faster than the *trans* compound, as the 1, 3 interactions engendered in the ground state is being released in the transition state or the transition state is more product-like.

Table 1. Dependence of rate of Tl(III) oxidation of cyclanols on substrate concentration.

[Tl(III)] = 0.0020 M; [H₂SO₄] = 0.90 M; Temp : 50° C. Solvent : 50% aqueous acetic acid.

Compound		$k_a \times 10^3$ litre-mole ⁻¹ sec ⁻¹
(a)	0.029	1.74
	0.051	1.77
	0.111	1.79
	0.153	1.80
	0.22	1.84
(b)	0.0047	66
	0.0094	66
	0.0148	66
	0.022	65
	0.026	68
(c)	0.0109	1.55
	0.043	1.54
(d)	0.0055	31
	0.020	31
(e)	0.033	10.4
	0.056	10.5

a = cyclopentanol ; b = cyclohexanol ; c = *trans*-2-chlorocyclohexanol ; d = cyclooctanol ;
e = borneol.

Table 2. Influence of varying acid concentration on Tl(III) oxidation of cyclohexanol [cyclohexanol] = 0.0060 M, [Tl(III)] = 0.0020 M, Temp. 50° C.
Solvent : 50% aqueous acetic acid.

[H ₂ SO ₄] M	$k_2 \times 10^2$ litre mole ⁻¹ sec ⁻¹
0.90	4.0
1.50	15.0
2.0	32

Table 3. Effect of added Mn(II) salt on Tl(III) oxidation of secondary alcohols
[Tl(III)] = 0.0020 M. Temp : 50° C : Solvent : 50% aqueous acetic acid.

	[Mn(II)] M	$k_2 \times 10^3$ litre mole ⁻¹ sec ⁻¹
(a)	—	1.80
	0.0080	1.78
	0.020	1.82
(b)	—	68
	0.0055	89
	0.0010	129
	0.0050	147
	0.020	179
(c)	—	2.1
	0.0010	2.1
	0.010	2.1

a = cyclopentanol ; b = cyclohexanol ; c = phenyl ethyl alcohol

Table 4. Ring size and reactivity pattern among the cyclanols in V(V) and Tl(III) oxidations Solvent : 50% aqueous acetic acid.

Compound	$k_2 \times 10^2$ litre mole ⁻¹ sec ⁻¹				
	A		B		
	55°C	40°C	45°C	50°C	55°C
Cyclopentanol	0.0117	0.106	0.166	0.186	0.55
Cyclohexanol	0.155	3.2	4.0	6.8	7.5
Cycloheptanol	0.023	0.28	0.98	1.20	...
Cyclooctanol	0.047	0.45	1.90	3.0	4.0
<i>Trans</i> -2-chlorocyclohexanol	...	...	0.109	0.175	0.28
<i>Trans</i> -2-phenylcyclohexanol	0.0057	...	...	3.0	5.3
<i>Cis</i> - <i>t</i> -butylcyclohexanol	...	...	...	1.55	...
<i>Trans</i> - <i>t</i> -butylcyclohexanol	...	...	...	0.95	...
Cyclohexanol- α -d	...	...	...	2.4	...

A : V(V) oxidation in 50% HOAc and 1.00 M H₂SO₄,

B : Tl(III) oxidation in 50% HOAc and in 0.90 M H₂SO₄.

2.4. Oxidation of bicyclo(2, 2, 1) heptan-2- ols

The kinetics of Tl(III) oxidation of isonorneol, borneol, endo(β) and exo(α)-norneols have been studied under the same conditions (table 5). The effect of bridging cyclopentane ring with two carbon bridge to form norbornane (bicyclo(2.2.1) heptane) is known to introduce considerable total angle strain (largely

Table 5. Comparative rate of Tl(III) oxidation of borneols and norborneols
[Tl(III)] = 0.0020 M, (H₂SO₄) = 0.90 M. Temp. 50° C. Solvent : 50% aqueous
acetic acid

Compound	$k_2 \times 10^3 \text{ litre mole}^{-1} \text{ sec}^{-1}$			
	45°C	50°C	55°C	60°C
borneol	...	53	...	...
isoborneol	5.5	10.7	22	...
exo- β -norborneol	...	2.6	3.2	8.0
endo- α -norborneol	...	0.74	1.46	...
cyclopentanol	1.66	1.86	5.4	...

edge in accentuating the puckering effect exercised by the cyclopentane molecule itself in order to reduce its energetically costly torsional interactions (Sargent 1966; Eliel 1962). Further, in exo-(β)-norborneol molecule an additional source of instability is the compression of van der Waals radii of the bridgehead (C₇) and the exo-hydroxyl group (C₂). The possible change in hybridisation when alcohol becomes ketone, from sp³ to sp², resulting in a considerably increased rate of oxidation of exo-(β)-norborneol over endo-(α)-norborneol and cyclopentanol (table 5). The increased reactivity of borneol and isoborneol over the norborneols, can be traced to the +I effect of three methyl groups facilitating the removal of secondary hydrogen as hydride ion. This may be transmitted through the series of σ -bonds or directly through space. Although definite answers are sometimes elusive, it is thought likely that through-space interactions predominate in norbornane and bornane systems, featuring carbonium ion centers (Story and Mark 1972). The driving force for the reaction may also be the formation of a strained product, ketone.

5. Kinetic isotope effect

The kinetic isotope effect, k_D/k_T , observed in the Tl(III) oxidation of cyclohexanol is 2.82 (table 4) whereas in the oxidation of benzhydrol it is 6.4 (Srinivasan and Venkatasubramanian 1974).

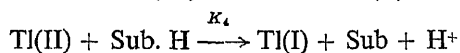
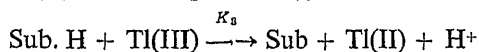
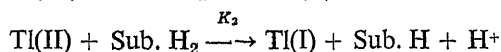
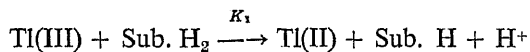
5. Temperature influence

The temperature effect on the rate of oxidation of alicyclic alcohols and borneols is determined between 45°C and 60°C (tables 4 and 5).

to a second order equation as

$$\text{rate} = K [\text{Ti(III)}] [\text{sub. H}_2],$$

can also be proposed (Srinivasan and Venkatasubramanian 1979). (Where K is a composite of different rate constants corresponding to chain propagating steps)



In most of the secondary alcohols, such as α -phenyl ethyl alcohol, benzhydrol and cyclopentanol, the chain propagating reactions are too rapid, acrylonitrile and Mn(II) do not intervene. Even in the V(V) oxidation of α -phenyl ethyl alcohol, the reaction mixture does not induce acrylonitrile polymerisation and a mechanism involving an electron deficient transition state, tending more towards carbonium ion character, has been proposed (Ganapathisundaram 1970). This also points to V(V) preferring one electron-transfer route in the case of cyclohexanol but probably not so in the case of α -phenyl ethyl alcohol. Only in the case of cyclohexanol the competition between the chain propagating species with acrylonitrile and Mn(II) are possible. Probably the one electron route $\text{Ti(III)} \rightarrow \text{Ti(II)} \rightarrow \text{Ti(I)}$ is more available for the strain free six membered ring than for the other cyclanols.

4. Experimental

Thallic oxide was dissolved in a mixture of acetic acid and sulphuric acid and was used as such after determining the concentration of Ti(III) by an iodometric procedure (Henry 1965). All other chemicals were of reagent grade and purified by conventional methods. Kinetic experiments were started by mixing equal volumes of the two reactants kept in a thermostat for about two hr. The reaction was followed by estimating the unreacted Ti(III) at various intervals by an iodometric procedure. The rate constants were evaluated using integrated equations or by least square plots of related quantities. The values reported were the average of at least two runs and were reproducible within $\pm 5\%$. The activation parameters were evaluated by least square plots of $\log k_2$ versus $1/T$. Mass spectrometry and NMR studies confirmed that the isotopic purity of cyclohexanol- α -d was 99%.

In the case of cyclopentanol, cycloheptanol and cyclooctanol, the corresponding ketones were formed as products whereas in the case of cyclohexanol, the cyclohexanole formed gets converted into cyclopentanecarboxylic acid (Wiberg and Evans 1960).

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on the mechanism of chiral aldol cyclization reaction

A SARKAR, H R Y JOIS, T R KASTURI * and D DASGUPTA[†]

Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012, India

[†]Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

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Abstract. Spectroscopic studies (¹H and ¹³C NMR, fluorescence and UV) of 2-[3-(*p*-methoxyphenyl)-3-ketopropyl]-2-methyl-cyclopentane-1,3-dione in the presence of *L*-amino acids and *L*-N-acetylphenylalanine ethyl ester indicated the possible involvement of a molecular association complex in the transition state of the amino acid catalyzed chiral aldolization of prochiral triketones to yield useful steroidal intermediates.

Keywords. Chiral intramolecular aldolization; molecular association; bifunctional catalysis; ¹³C and ¹H NMR; fluorescence quenching; ultra violet; hydrogen bonding; noncovalent interaction.

Introduction

The chiral aldol cyclization of the prochiral triketone (1) to the chiral diketone (2) has been utilized in a number of recent steroid syntheses (Cohen 1976 and references therein; Shimizu *et al* 1980) employing naturally occurring amino acids and their derivatives as the chiral catalysts. The mechanism of the transformation is still uncertain, although a few probable modes have been suggested. In an earlier review, (Sarkar *et al* 1979) we pointed out the discrepancies in the postulated enamine intermediate (Danishefsky and Cain 1976) because it does not explain (a) lack of efficient chiral induction by amino acid derivatives * although they possess the same chirality as that of the parent amino acids; (b) role of free carboxylic function in chiral recognition or participation in the chemical process and (c) enhanced chiral induction with amino acids possessing side chains of similar dimensions as that of the acyclic portion of the triketone. It was therefore conten-

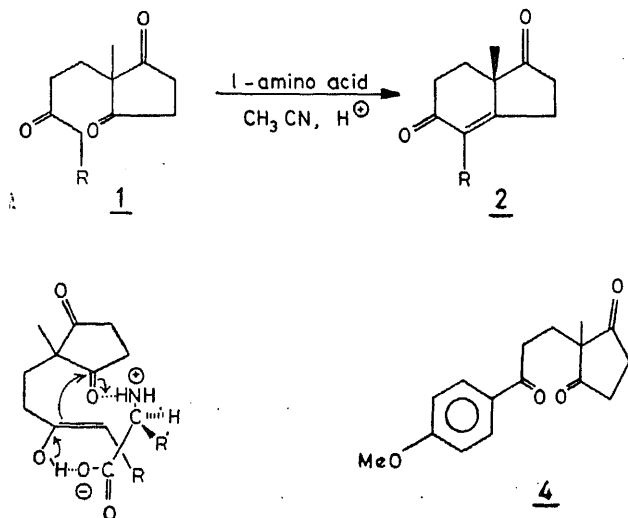
To whom all correspondence should be addressed.

Synthetic studies with *L*-histidine methylester hydrochloride, *L*-dehydroabietylamine and brucine catalysts in the cyclization of 1 (R = CH₃) also indicated that a chiral amine providing a chiral

ded that bifunctional catalysis involving a molecular association between the substrate and the catalyst would be a more probable mechanism; the free energy of activation associated with the transition state could be largely compensated by molecular complexation (catalysis) and the chiral bias could be due to the chirality of the catalyst. The transition state has been schematically represented as 3. The mechanism accounts for (a) less degree of chiral induction with amino acid derivatives; (b) role of the Zwitterionic structure of the amino acid in the catalytic function and (c) the recognition of residual (nonfunctional) segments of the amino acid and the substrate for greater chiral induction. This paper deals with the results of the spectroscopic studies carried out to investigate the presence and the nature of the intermediate species and their role in this chiral transformation.

2. Design of model substrate

It was recognized at the outset that while the structure of an intermediate could be studied conveniently by spectroscopic techniques, a transition state involving bifunctional catalysis would not be amenable for such direct observations. Hence a substrate (4) (Buchowieski and Zajac 1979) was synthesized such that the intermediate or molecular complex could be formed, but further reaction leading to the formation of the product was precluded by the absence of a centre for cyclization. The molecule (4) possessed all the functionalities of the triketone (1) to facilitate the formation of a related intermediate or molecular complex, while the aromatic group in the triketone (4) provided an ideal internal probe to be monitored by spectroscopic techniques. The tacit assumption was that the specific conformation of the intermediate or complex thus identified, would satisfactorily approximate the geometry of the transition state structure.



Diethylamino-*p*-methoxy-acetophenone (7.8 g) and 2-methylcyclopentane-1,3-dione (4.2 g) in 40 ml of xylene containing 10 ml of pyridine was heated under reflux for 24 hr. The solution was cooled, diluted with chloroform, washed with 5% HCl, water, aq. NaHCO₃ and water and dried over anhydrous Na₂SO₄. The solvent was removed and the residue crystallized from hexane-benzene to furnish the triketone (4) as a white crystalline solid, m.p. 101° (6.3g, 69%). IR(nujol): ν_{max} 1770, 1725, 1675, 1615 and 1580 cm⁻¹; NMR (CDCl₃): δ 1.20 (s, CH₃, 3H), 1.03 (t, —COCH₂CH₂—, 2H, J = 7 Hz) 2.83 (s, ketomethylenes, 4H), 2.92 (t, —COCH₂CH₂—, 2H, J = 7 Hz), 3.83 (s, Ar—OCH₃, 3H), 6.90 (d, Ar—H, 2H, J = 9 Hz), 7.86 (d, Ar—H, 2H, J = 9 Hz). Concurrent to our work, a patent describing the preparation of this compound was published, which was noted in a subsequent publication (Kasturi *et al* 1982) from our laboratory.) Analysis: C 69.68, H 6.87; C₁₆H₁₈O₄ requires C 70.05, H 6.61%.

2. Spectroscopic studies

Although the cyclization reactions were generally carried out in CH₃CN or DMF in the absence of water, an 80% (v/v) CH₃CN—H₂O (CD₃CN—D₂O for NMR) solvent mixture was used throughout the spectral study. The addition of water to the medium was necessary due to the low solubility of amino acids in organic solvents, while the possible disruption of the balance between the hydrogen bonding and the hydrophobic association restricted the amount of water added.

The ¹³C NMR spectra were recorded in a Bruker 270-WH FT NMR machine operating at 67.89 MHz) in CD₃CN—D₂O (80%, v/v) solution containing TMS as the internal standard. The broad-band decoupled spectrum was obtained with proton noise decoupling at 270 MHz while the off-resonance decoupled spectrum was recorded with single frequency irradiation at *ca.* -5 δ (highfield region from TMS) with the decoupler power of *ca.* 2 watts and pulse interval of 3 sec. The emission spectra of *l*-phenylalanine and *l*-N-acetylphenylalanine ethyl ester were recorded in the presence of various concentrations of the triketone (4) in Perkin-Elmer fluorimeter Model MPF-44.

The ¹H NMR spectra were recorded on a Varian T-60 machine with CD₃CN—D₂O (80%, v/v) as the solvent using TMS as the internal standard.

The UV spectra were recorded in a Beckmann UV and visible recording spectrophotometer Model 26 using CH₃CN—H₂O (80%, v/v) as the solvent. The reference solution always contained equal amount of the amino acid component to cancel the additive contribution to the absorbance of the sample under study.

Results and Discussion

The ¹³C NMR spectrum of the compound (4) exhibited two distinct carbonyl signals, well separated for identification. On addition of the amino acid, the formation of the intermediate should be directly observable by the emergence

study of the interaction between pyridoxal and *l*-alanine and reported in the literature : see Jo *et al* 1977). In this case, a gradual downfield shift of the carbonyl carbon with the emergence of no new shielded carbon signal was observed for the triketone (4) in the presence of different quantities of *l*-phenylalanine (this amino acid was chosen for maximum nonbonding stabilizing interaction in the complex or the intermediate). It was confirmed from the peak print-out that the signals of all other carbons of the compound (4) remained almost unaltered while the carbonyl signals were shifted downfield consistently (table 1). Absence of new signals ruled out the presence of carbinolamine/Schiff's base/enamine in the solution—a fact also supported by the uv studies, as described later. The observed downfield shift was therefore attributed to hydrogen bonding (Stothers 1972) involving the carbonyl groups and the protonated amino function of the amino

Table 1. Changes in the chemical shifts of different carbons of (4) (0.9 M) in the presence of different concentrations of *l*-phenylalanine in CD₃CN-D₂O (80%, v/v) with TMS = 0 ppm.

Concentration of <i>l</i> -phenylalanine (M)	$\Delta\delta$					
	5-membered ring carbonyl	P-OMe-Ar- CO	Ar-C-OMe	Ar-OCH ₃	Ring methylenes	Angular methyl
	$\delta = 218.805$	$\delta = 199.894$	$\delta = 164.677$	$\delta = 56.328$	$\delta = 35.620$	$\delta = 19.003$
0.09	+ 0.496	+ 0.186	- 0.031	+ 0.032	- 0.031	0
0.12	+ 0.741	+ 0.378	+ 0.031	+ 0.029	0	+ 0.031
0.15	+ 1.674	+ 0.744	+ 0.062	+ 0.031	0	+ 0.093

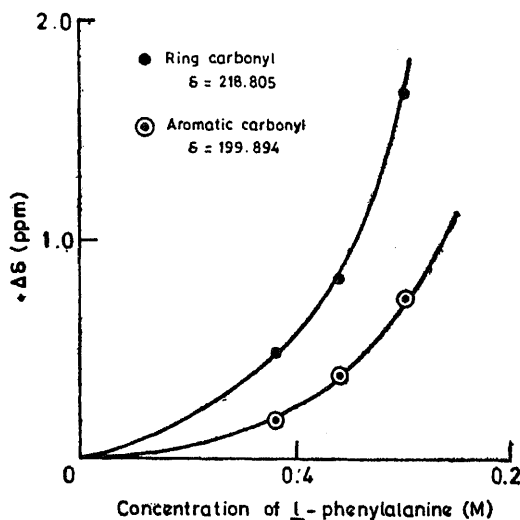


Figure 1. Change in the chemical shift of the carbonyl signals of the compound (4) with different concentrations of *l*-phe.

1. This further indicated that the complexation is a fast exchanging process on the NMR time scale. The comparatively large shift noticed for the cyclopentanone carbonyl signal indicated a preferential binding at that site (figure 1). If the hydrogen bonding envisaged above is significant in the stabilization of the complex, the prevention of efficient hydrogen bonding would definitely impair complex formation. Thus, quenching (Udenfriend 1962) of an amino acid, phenylalanine (which permits both hydrogen bonding and nonbonding interaction) would proceed with a higher efficiency than an amino acid derivative, *N*-acetylphenylalanine ethyl ester (which permits nonbonding interaction but not hydrogen bonding) with the same substrate (4). The fluorescent properties of these two substances were studied in the presence of various concentrations of the triketone (4), a nonfluorescent compound. The results are shown in figure 2. In both the cases, there had been progressive quenching with the increasing concentration of the triketone (4). The plots for the quenching process indicated comparable quenching efficiency in both the cases. This observation implied the formation of a charge-transfer complex in the excited state, probably resulting from the stacking of the aromatic rings. Such a position evidently called for a considerable proximity of the two aromatic rings in the complex, though the importance of hydrogen bonding for the complex formation was not definitely reflected in the above observations.

The 60 MHz ^1H NMR spectra of the triketone (4) in the presence of *L*-phenylalanine further corroborated the stacking phenomenon in the ground state. The stacking interaction results in an upfield shift of the aromatic proton signals (Chan *et al* 1964). This was observed for the aromatic signals of both the molecules (figure 3). The decrease in the absorbance of the chromophoric group in the substrate in the presence of an added reagent had been used as a criterion for the complex

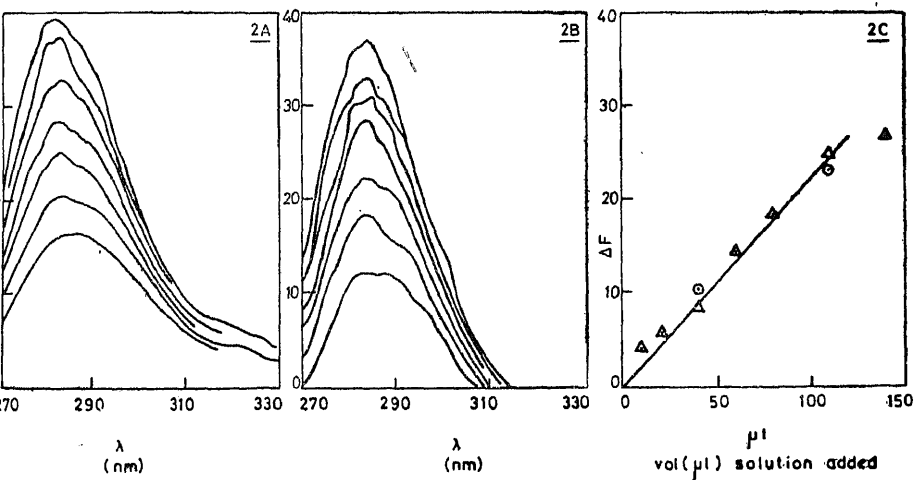


Figure 2. (A) The emission spectra of *L*-phe (3×10^{-4} M) excited at 257 nm in presence of various volumes of added (4) (B) The emission spectra of the *L*-phe ester amide (3×10^{-4} M) excited at 257 nm in presence of various volumes of added (4) (C) The plot of change of fluorescence intensity (ΔF) versus volume of addition of



Figure 3. The 60 MHz ^1H NMR Spectra (low field region) of the triketone (4) (0.4 M) in $\text{CD}_3\text{CN}-\text{D}_2\text{O}$ (80%, v/v) in the presence of (i) 0.05 M *L*-phe (—) (ii) 0.15 M *L*-phe (---). The peak marked asterisk corresponds to the aromatic proton of *L*-phe.

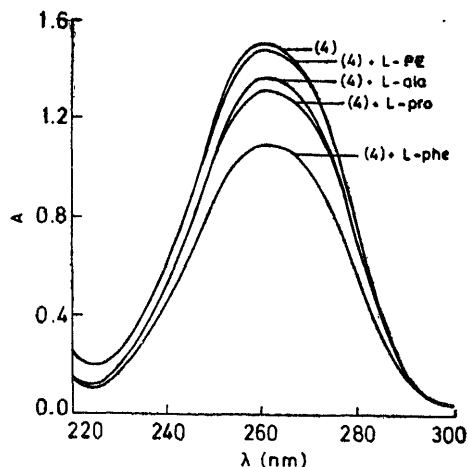


Figure 4. The UV spectra of the triketone (4) alone (0.8×10^{-4} M) and in the presence of amino acids (2.0×10^{-4} M). PE = *N*-acetyl phenyl alanine ethyl ester.

formation between the two (Eisenberg and Crothers 1979). To assess the relative importance of the hydrogen bonding and the nonbonding interaction in stabilizing the complex, a comparative study of the UV absorbance of different mixtures of triketone (4) with various amino acids and an amino acid derivative, was undertaken (1 : 2 M) (figure 4). The decrease in the absorbance without any significant change in the spectra recorded under identical conditions again confirmed the absence of a discrete intermediate and the presence of a molecular association complex. The decrease in the absorbance was maximum for *L*-phenylalanine, while for others it was much less significant. The greater change in the absorbance was indicative of a stronger complexation between the triketone (4) and *L*-phenylalanine, stabilized both by hydrogen bonding and nonbonding interaction.

5. Conclusion

The present investigation demonstrated (a) no intermediate carbinalamine/Schiff's base/enamine was formed between the triketone (4) and the amino acid, (b) a molecular complex stabilized both by hydrogen bonding and nonbonding interactions was definitely formed under the reaction condition of aldol cyclization (such nonbonding interactions contributing to the specific orientation of the molecules in hydrogen bonded association complexes in nonpolar solvents, was demonstrated earlier; see Breslow 1972) and, (c) the hydrogen bonding was crucial for the formation of a stable complex, while the stacking interaction alone could not bring about a complexation of appreciable stability.

Thus, assuming the factors operative in the stabilization of the above molecular complex under the simulated reaction condition are practically the same as those relevant for the transition state of the chiral intramolecular aldolization, the above observation is in favour of the proposition of bifunctional catalysis as depicted in 3. The manifestation of a molecular complexation catalyzing intramolecular chiral cyclization, to the best of our knowledge, is identified for the first time in the present case.

Acknowledgement

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Synthesis of 2-aryl-3-(3-disubstituted aminomethyl-2-thio-4-oxo-thiazolidin-5yl)-methylene-yl-indoles as CNS active agents

CHAPLA CHAUDHARY, RAJESH AGARWAL and
V S MISRA*

Department of Chemistry, Lucknow University, Lucknow 226 007, India

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Abstract. A new series of the title compounds has been synthesised and their lethal and gross CNS activities on the brain of albino mice investigated. The intermediate 2-aryl-3-(3-thio-4-oxo-thiazolidin-5yl)-methylene-yl indoles (1-3) were prepared by the 'Knoevenagel Condensation' of 2-thio-4-oxo-thiazolidine with 2-aryl-indol-3-aldehydes. The aforesaid compounds (1-3) gave fifteen new title 2-aryl-3-(3-disubstituted aminomethyl 2-thio-4-oxo-thiazolidin-5yl)-methylene-yl-indoles (4-18) by the 'Mannich reaction' with different secondary amines, utilising the thio-amidic active hydrogen at position-3 of thiazolidine ring. The structures of all the newly synthesised compounds have been assigned by their elemental analysis (C, H, N) and spectral studies (IR and PMR). In their pharmacological screenings, the compounds were found to be psychotropics and relatively nontoxic except one compound. Few of the tested compounds have induced writhing and showed effect on the body temperature.

Keywords. Thiazolidinyl-methylene-yl-indoles; Mannich reaction; psychotropics; CNS depressants; CNS stimulants; writhing.

Introduction

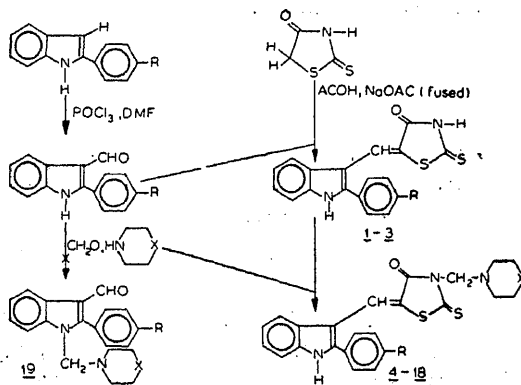
A large number of indole derivatives are known to effect different biological effects. Serotonin, an indole derivative, is a neurohumoral transmitter (Hertzler 1970). The investigations, regarding the activities of serotonin and its precursor, 5-HT, on the mental illness, show that serotonin is somehow related to anticonvulsants, as the serotonin level in brain is increased by various anticonvulsants (Gado and Isaacson 1970). Further, a wide number of indole derivatives are reported to have valuable therapeutic effectiveness for the cure of convulsions (Leslie and Willette 1964), CNS depressions (Tachikawa *et al* 1977) and MAO inhibition (Allmany *et al* 1966) along with their antidepressant (Warner Lamber 1980) and CNS blocking (Pigerol *et al* 1978) properties. On the other hand, thiazolidin-2-thione derivatives are known to possess psychotropic properties

(Agarwal *et al* 1980). It is also worth mentioning that 'Hydantoin', a well-known anticonvulsant and CNS depressant nucleus (Waser *et al* 1978), is a close structural analogue of thiazolidin-2-thione, differing only in that N-H at position-1 and oxygen of C=O at position-2 replace the sulphur atoms. Moreover, different secondary amines like morpholine, piperidine and N-substituted piperazines are also known to impart a variety of effect on the CNS disorders (Kojima *et al* 1978 ; Kubela *et al* 1978 ; Weber *et al* 1979).

The aforementioned literature reports prompted the authors to synthesise fifteen new title indole derivatives and to subject them for toxicity test and gross Central Nervous System (CNS) screening on the brain of albinomice. In this connection some 2-aryl-3-(2-thio-4-oxo-thiazolidin-5yl)-methylene-indoles (1-3) were synthesised by the Knoevenagel condensation between the aldehydic group of 2-aryl indol-3-aldehydes and active methylenyl group of 2-thio-4-oxo thiazolidine, using acetate ion as a mild base (a fundamental necessity for such a type of reaction). The cyclo-thio-amidic active hydrogen at position-3 was blocked by the Mannich reaction with different secondary amines in aqueous formaldehyde solution (40%) to form a methylene bridge, to furnish the title compounds (4-18).

It is noteworthy that during the Mannich reaction, the disubstituted amino-methyl group goes at position-3 of thiazolidin nucleus not at position-1 of indole, which was confirmed by the lack of downfield band of former N-H in the IR and PMR spectra of title compounds. This is further supported by the fact that when plain 2-aryl-indole-3-aldehyde was subjected to Mannich reaction under similar conditions and with the same amines, it didn't give the desired N¹-disubstituted aminomethyl congener. The obtained compound was identified as the starting one. The failure of reaction is presumably due to the steric hindrance by the adjacent aryl group at position-2 of indole.

The current paper deals with the synthesis and CNS activities of these compounds along with their toxicity. The synthetic route is as follows:



to evaluate the lethal values, the compounds were administered, at different doses as 464 and 1000 mg/kg weight of mice, intraperitoneally as a suspension of in an acacia and the approximate lethal doses in 50% of the tested animals (ALD_{50}) were determined by a standard method (Weil 1952).

For their effect on the CNS, they were finally introduced in albino mice, by the similar aforementioned procedure, at 1/5th of their ALD_{50} and changes in their spontaneous motor activity (SMA) and reaction to sound, touch and body temperature were recorded. To substantiate these gross CNS observations, mobility counts were noted, at time intervals of 1/2, 1, 2 and 3 hr after the compound's administration, using an actophotometer equipped with photocells.

Results and discussion

The results of the study of toxicity test and gross CNS observations are cited in table 1. All the compounds were found to be quite nontoxic except compound 13 (ALD_{50} : 316 mg/kg). It was observed that some of the title compounds were found to be CNS depressants while others were stimulants, as they decreased or increased the SMA and reactivity respectively. Few of the compounds induced twisting (twisting of belly) and on this basis, they may be tried as muscle relaxants. The compounds have also shown marked effect on the body temperature. Moreover, from the structure and pharmacological data of the final products, a definite structure activity relationship has been drawn, which is summarised as follows :

(i) The substitution at para position to phenyl ring, present at position-2 of indole, showed a wide role on the CNS effects of the compounds, viz., the compounds without any substitution at that position were CNS depressants whereas the methyl and chloro analogues were found to be stimulant on the CNS.

(ii) From the data of mobility counts after 3 hr of the compounds injection it appears that :

(a) The N-phenyl piperazino derivatives have the highest depressant (compound 7, 46.72%) and lowest stimulant (compounds 13 and 17 respectively, 1.45 and 0.72%) effects in their groups of five. From these results it was presumed that the presence of CH_3 or Cl group at para to phenyl ring has increased the mobility counts for compounds 13 and 17, in the same trend as is observed in the remaining compounds (9-18), but due to the highly depressant nature of N-Ph piperazino group, the compounds 13 and 17, have overcome the stimulant nature of CH_3 and Cl groups and thus have the lowest stimulant nature.

(b) On the other hand, the morpholino congeners have shown the reversed activities as compared to the aforesaid findings, viz., the morpholino derivatives have the lowest depressant (compound No. 4, 2.92%) and highest stimulant (Nos. 9 and 14 respectively, 28.46 and 14.59%) effects in their groups of five.

(iii) It is also worth mentioning that the compounds, which were grossly CNS depressants have also decreased the body temperature (hypothermia by

Table 1. ALD₅₀ and gross CNS observations of the compounds 4-18 at 1/5th of their ALD₅₀.

ALD ₅₀ mg/kg (i.p.)	Gross CNS observations			Mobility counts						Depressant Stimulant	
	SMA & reactivity	Death	Writhing	Change in body temp. (°C)	0 hr	½ hr	1 hr	2 hrs	3 hrs	activity (%)	activity (%)
					C	181	158	146	137		
					T						
681	↓	0/5	(-)	↓ 0.4	233	152	146	143	133	2.92	(-)
681	↓	0/5	(-)	↓ 0.4	238	168	139	142	119	13.14	(-)
>1000	↓	0/5	(+)	↓ 0.5	232	139	140	130	118	13.87	(-)
1000	↓	0/5	(+)	↓ 0.8	206	115	143	125	73	46.72	(-)
>1000	↓	0/5	(+)	↓ 0.3	206	90	135	120	111	18.98	(-)
>1000	↑	0/5	(+)	↑ 0.4	265	242	202	189	176	(-)	28.46
681	↑	0/5	(-)	↑ 0.1	268	169	241	176	151	(-)	10.21
>1000	↑	0/5	(-)	↑ 0.9	241	184	171	156	142	(-)	3.64
>1000	↑	0/5	(-)	(-)	235	170	163	148	139	(-)	1.45
316	↑	0/5	(-)	(-)	263	179	161	153	149	(-)	8.75
>1000	↑	0/5	(-)	1.1	252	192	177	164	157	(-)	14.59
681	↑	0/5	(+)	↑ 1.6	253	188	167	151	143	(-)	4.37
1000	↑	0/5	(+)	↑ 0.1	230	181	167	154	145	(-)	5.83
>1000	↑	0/5	(+)	↑ 0.6	229	173	147	142	138	(-)	0.72
>1000	↑	0/5	(+)	↑ 0.2	241	172	168	157	146	(-)	6.56

sed, ↓ = Decreased, (+) = Present, (-) = Not effected, temp. = temperature, C = Controlled, T = Treated.

uncorrected. IR spectra in KBr phase were recorded on a Perkin-Elmer 157 and 177 spectrophotometers ($\nu_{\max}$ in cm^{-1}) and PMR spectra in $\text{DMSO}-d_6$ or CDCl_3 on a varian A60D instrument using TMS as internal standard (chemical shift in δ ppm). Purity of the compounds was checked by TLC using silicagel-G coated (0.25 mm) plates and benzene-ethanol (100 : 5) as irrigant.

4.1. Synthesis of 2-thio-4-oxo-thiazolidine

It was prepared by the method of Julian and Bernard (1935).

4.2. Synthesis of 2-aryl-indol-3-aldehydes

The desired aldehydes have been prepared according to the method of Weisbach *et al* (1964).

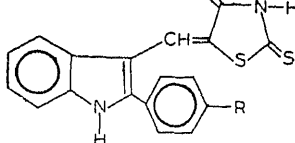
4.3. Synthesis of 2-(4-chlorophenyl)-3-(2-thio-4-oxo-thiazolidin-5yl)-methylenyl-indole (3)

A mixture of 2-(4-chlorophenyl)-indol-3-aldehyde (0.01 mol), 2-thio-4-oxo-thiazolidine (0.01 mol) and fused sodium acetate (5 g) in glacial acetic acid (50 ml) was refluxed for 4 hr on a wire gauze with occasional shaking. Thereafter, it was cooled and poured with stirring in ice-cold water (200 ml). The condensation product obtained was filtered, washed well with water and recrystallised from dioxane, m.p. 238°C , yield 85%. Analysis : Found : C, 58.33 ; H, 3.01 ; N, 7.62, $\text{C}_{18}\text{H}_{11}\text{ON}_2\text{S}_2\text{Cl}$. Calc. : C, 58.29 ; H, 2.96 ; N, 7.55% ; IR : 3400, 3200 (N-H str for thiazolidine and indole moieties respectively), 3050, 2900 (C-H, Ar and Ali), 1690 (N-C=O), 1600 (N-H bending) and 1220 (C=S) ; PMR : 9.82 (s, 1H, N-H of thiazolidine), 8.1 (s, 1H, N-H of indole) and 7.72-7.05 (m, 9H, 8Ar-H and 1 -C=C-H). The downfield position of N-H of thiazolidine in IR and PMR was expected to be due to the presence of C=O and C=S groups adjacent to N-H.

Similarly other compounds (1, 2) of the series were prepared and are listed in table 2.

4.4. Synthesis of 2-phenyl-3-[3-(4-phenyl piperazino) methyl-2-thio-4-oxo thiazolidin-5yl]-methylenyl-indole (7)

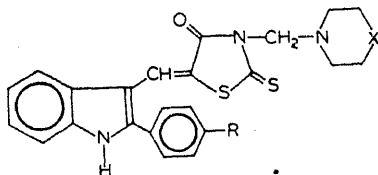
To a suspension of 2-phenyl-3-(2-thio-4-oxo thiazolidin-5yl)-methylenyl-indole (0.0025 mol) in warm ethanol (20 ml), formaldehyde solution (37%, 1 ml) was added. To the resulting suspension, N-phenyl piperazine (0.0025 mol) was added with constant vigorous stirring and the solution then again heated. Thereafter the reaction mixture was kept aside for 24 hr and the product that separated out was filtered, washed with pet ether ($60-80^\circ$) and recrystallised from ethylacetate, m.p. 194°C , yield 90%. Analysis : Found : C, 68.19 ; H, 5.16 ; N, 10.91 ; $\text{C}_{29}\text{H}_{26}\text{ON}_4\text{S}_2$. Calc. : C, 68.23 ; H, 5.09 ; N, 10.98% ; IR : 3200 (N-H of indole), 3050, 2900



Sl. No.	R	m.p. (°C)	Molecular formula ^a	Yield (%)	% Nitrogen	
					(Calcd.)	(Found)
1.	H	>250	C ₁₈ H ₁₂ ON ₂ S ₂	90	8.33	9.39
2.	CH ₃	245	C ₁₉ H ₁₄ ON ₂ S ₂	85	8.00	7.92
3.	Cl	238	C ₁₈ H ₁₁ ON ₂ S ₂ Cl	85	7.55	7.62

^a All the compounds recrystallised from dioxane, gave correct analysis for C and H too.

Table 3. 2-aryl-3-(3-disubstituted aminomethyl-2-thio-4-oxo-thiazolidin-5-yl)-methylenyl-indoles.



Sl. No.	R	X	m.p. (°C)	Molecular formula ^a	Yield (%)	% Nitrogen	
						(calcd.)	(found)
4.	H	[O]	204	C ₂₃ H ₂₁ O ₂ N ₃ S ₂	90	9.65	9.52
5.	H	CH ₃	232	C ₂₄ H ₂₃ ON ₃ S ₂	87	9.69	9.61
6.	H	N-CH ₃	219	C ₂₄ H ₂₄ ON ₄ S ₂	85	12.50	12.43
7.	H	N-C ₆ H ₅	194	C ₂₉ H ₂₆ ON ₄ S ₂	90	10.98	10.91
8.	H	N-C ₆ H ₄ CH ₃ (4)	200	C ₃₀ H ₂₈ ON ₄ S ₂	93	10.68	10.66
9.	CH ₃	[O]	174	C ₂₄ H ₂₃ O ₂ N ₃ S ₂	85	9.35	9.30
10.	CH ₃	CH ₃	188	C ₂₅ H ₂₅ ON ₃ S ₂	83	9.39	9.19
11.	CH ₃	N-CH ₃	194	C ₂₅ H ₂₅ ON ₄ S ₂	90	12.12	11.98
12.	CH ₃	N-C ₆ H ₅	194	C ₃₀ H ₂₈ ON ₄ S ₂	85	10.68	10.46
13.	CH ₃	N-C ₆ H ₄ CH ₃ (4)	148	C ₃₁ H ₃₀ ON ₄ S ₂	90	10.40	10.51
14.	Cl	[O]	271	C ₂₃ H ₂₀ O ₂ N ₃ S ₂ Cl	79	8.94	9.01
15.	Cl	CH ₃	270	C ₂₄ H ₂₂ ON ₃ S ₂ Cl	80	8.98	8.76
16.	Cl	N-CH ₃	180	C ₂₄ H ₂₃ ON ₄ S ₂ Cl	82	11.60	11.91
17.	Cl	N-C ₆ H ₅	262	C ₂₉ H ₂₆ ON ₄ S ₂ Cl	85	10.28	10.05
18.	Cl	N-C ₆ H ₄ CH ₃ (4)	260	C ₃₀ H ₂₇ ON ₄ S ₂ Cl	90	10.02	10.32

^a All the compounds, recrystallised from ethyl acetate, gave correct analysis for C and H too.

C-H Ar and Ali), 1690 (N-C=O), 1590 (N-H bending) and 1220 (C=S) ; PMR : 3.02 (s, 1H, N-H of indole), 7.7-6.7 (m, 15H, 14 Ar-H and 1-C=C-H), 5.02 (s, 2H, N-CH₂-N), 3.09 (t, J = 2.9Hz, 4H, -CH₂-N-CH₂) and 2.92 (t, J = 2.9Hz, 4H, -CH₂-N-CH₂).

$$\begin{array}{c} \text{C}_6\text{H}_5 \\ | \\ \text{H, -CH}_2\text{-N-CH}_2\text{).} \\ | \\ \text{CH}_2 \end{array}$$

The other compounds of the series were prepared in a similar manner. Their results are listed in table 3.

5. Attempted preparation of N¹-(4-phenyl piperazino) methyl-2-phenyl-indol-3-aldehyde (19)

A mixture of 2-phenyl-indol-3-aldehyde (0.0025 mol) and 4-phenyl piperazine (0.0025 mol) in ethanol (20 ml) containing aqueous formaldehyde solution (1 ml) was heated on the water bath for 10 min. The reaction was kept aside for 24 hr. Thereafter, it was concentrated to get the solid product, which was analysed by TLC and identified (m.p., m.m.p.) as the starting one.

Acknowledgement

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Electrochemical studies on cobalt tris (acetylacetonate)

R. J. MAGEE* and BOOKHARI ANNUR

Department of Inorganic and Analytical Chemistry, La Trobe University, Bundoora 3083, Victoria, Australia

MS received 19 October 1982

Abstract. The electrochemical reduction of cobalt acetylacetonate ($\text{Co}(\text{acac})_3$) at the mercury electrode in propylene carbonate and DMSO has been carried out using dc polarography, controlled potential coulometry, chronoamperometry and cyclic voltammetry. In propylene carbonate, polarograms showed two well defined waves, one wave being an adsorption pre-wave, the other an irreversible, diffusion-controlled electron transfer process. From chronoamperometry the diffusion coefficient was determined. Cyclic voltammetry confirmed the polarographic results, although additional adsorption waves were found. In DMSO, results were similar to those in propylenecarbonate. However, polarograms showed no adsorption pre-wave and additional adsorption waves found in propylene carbonate in the cyclic voltammograms were absent. The mechanism of the reduction process in both solvents is discussed.

Keywords. Cobalt tris (acetylacetonate) ; electrochemical studies ; dimethyl sulphoxide ; propylene carbonate.

1. Introduction

During electrochemical studies on mixed ligand complexes of transition metals, where the mixed ligands were β -diketonates and monothiocarbamates, it was necessary to check the literature for reported work on the transition metal β -diketonates complexes in order that the complex electrochemistry of the mixed-ligand complexes might be elucidated. Surprisingly, there was found to be a lack of information on this type of complex. Patterson and Holm (1972) found that Ru(III) β -diketonates showed uncomplicated polarographic behaviour in DMF or acetonitrile at the platinum electrode with current-voltage curves indicative of reversible or quasi reversible, one electron transfer reactions. $E_{1/2}$ values were very strongly influenced by the nature of the chelate ring substituents.

The case of reduction increased as the number and type of electron-releasing substituents were decreased. It was concluded that, for the Ru(III) complexes,

* To whom all correspondence should be addressed,

present work, the electrochemical behaviour of cobalt (acac)₃ in propylene carbonate and DMSO at the mercury electrode was investigated.

2. Experimental section

2.1 Preparation of cobalt tris (acetylacetonate)

The complex was prepared in a manner similar to that by Bryant and Fernelius (1957). A mixture of 5g CoCo₃ and 40 cm³ of acetylacetone in a 250 cm³ conical flask was heated to 90–95° C. The mixture was stirred rapidly with a magnetic stirrer, while 60 cm³ of 10% H₂O₂ was added dropwise: the addition required about 45 min, the temperature being maintained at 90–95° C. At the end of the reaction, the liquid layer was an intense green colour and a quantity of green solid deposited. The mixture was chilled to –10° C in an ice/salt bath to precipitate any further product, followed by filtering on a Buchner funnel. The crystals were dried at 110° C for 20 min and boiling benzene added until the crystals just dissolved. 300 cm³ of petroleum ether was added slowly (over a period of 3 min) to the warm benzene solution and the mixture cooled in an ice/salt bath. The resulting product was filtered and air-dried.

2.2 Analytical data

Tris (acetylacetonato) Co(III) :	m.p. 210° C (lit. value 213° C).
Calcd (for C ₁₅ H ₂₁ O ₆ Co) :	C, 50.7 ; H, 5.94
Found :	C, 50.49 ; H, 5.98.

Propylene carbonate was purified by reduced pressure distillation at 120–130° C. Distillation was carried out twice, with collection of the middle 60% fraction. It was stored in a dark bottle over type 5A molecular sieve. DMSO was purified by vacuum distillation of the bulk material, the middle fraction being collected. It was stored over molecular sieves.

A Princeton Applied Research (PAR) model electrochemistry system was employed for the polarographic (dme), the cyclic voltammetric (hmde) and the chronoamperometric (hmde) studies. All potentials were measured against Ag/AgClO₄ (0.02 M)/NaClO₄ (0.2 M) reference electrode in propylene carbonate or DMSO. Supporting electrolyte used was 0.2M NaClO₄. The reference electrode potentials were checked daily against an aqueous Ag/AgCl(s)/KCl(satd) electrode. The auxiliary electrode was platinum. For constant potential coulometry with a mercury-pool electrode (diameter 4.6 cm), a Beckman Electroscan 30 instrument was employed. All electrochemical measurements were carried out at 25 ± 0.2° C, the solution being degassed with pre-dried, oxygen-free nitrogen,

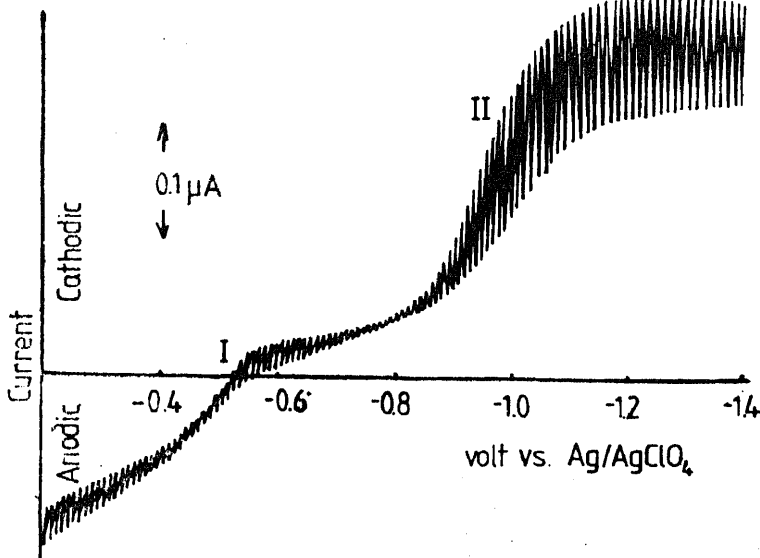


Figure 1. Polarogram of $\text{Co}(\text{acac})_3$ (1.00 mM) in propylene carbonate with 0.1 M NaClO_4 and 0.008% TRX-100 ($T = 25^\circ \text{C}$; Hg height = 67.5 cm).

Results and Discussion

D. C. polarography and controlled-potential coulometry

In propylene carbonate, polarograms showed two well-defined waves (figure 1) with $E_{1/2}$ values of $-0.497 \pm 0.006 \text{ V}$ (wave I) and $-0.980 \pm 0.006 \text{ V}$ (wave II) against the Ag/AgClO_4 (0.02 M), NaClO_4 (0.2 M) reference electrode.

The limiting current, i_d , of wave I was found to be independent of concentration, whereas that of wave II was essentially proportional to concentration. The effect of varying the height of the mercury showed a linear increase of limiting current with increase in mercury height for wave I, while $i_d h_{\text{corr}}^{-1/2}$ was essentially constant for wave II. The observations appear to imply that wave I is an adsorption wave and wave II is a diffusion-controlled electron transfer process. Further, the temperature coefficient of $1.4 \pm 0.3\%$ per degree for wave II over the temperature range $25-48^\circ \text{C}$ is consistent with a diffusion-controlled process (Meites 1965).

The log-plot analysis of wave II showed marked curvature with initial slope 0.095 and a final slope of 0.149, indicating departure from reversible behaviour for the electron-transfer process. Cathodic controlled potential coulometry was carried out at -0.7 V , i.e., on the plateau of wave I and gave a zero value for ' n ', confirming the absence of a reduction process. On the other hand, cathodic coulometry on the plateau of wave II (-1.2 V) gave the following results in 2 separate determinations:

1.078×10^{-5}	0.9545	0.92
4.968×10^{-6}	0.4698	0.98
6.933×10^{-6}	0.6370	0.95

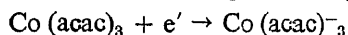
Wave II, therefore, represents a reduction process involving one electron.

The effect of water on the reduction process was examined. It was found that the limiting current for wave II was independent of water concentration up to 10M. However, above 1M concentration of water, there was a slight shift of $E_{1/2}$ towards more positive potentials.

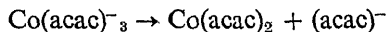
The effect of free ligand was investigated by the addition of sodium acetylacetonate to a solution of $\text{Co}(\text{acac})_3$ containing 0.008% TRX-100. Polarogram showed a very marked increase in the height of wave I, with little or no effect on wave II. This indicates that wave I has associated with it an anodic reaction depending on the concentration of free ligand (Meites 1965). The likely reaction is the oxidation of mercury in the presence of acetylacetonate anions.

Anodic coulometry was carried out on a solution of sodium acetylacetonate at -0.2 V with supporting electrolyte present. UV spectra were also recorded at various intervals over several hours. The latter showed steady depletion of the ligand in solution. At the same time, a whitish precipitate confirmed that $\text{Hg}(\text{acac})_2$ was produced. For the anodic coulometry, the number of electrons involved in the anodic process was one, indicating an anodic reaction produced by the oxidation of mercury in the presence of acetylacetonate ligand.

During controlled-potential coulometry of a 0.25 mM $\text{Co}(\text{acac})_3$ solution at -1.2 V, in the presence of supporting electrolyte, UV spectra were recorded at hourly intervals. Initially, the spectrum was that of $\text{Co}(\text{acac})_3$. However, as electrolysis proceeded, a new spectrum continued to develop which was found to be identical to that for $\text{Co}(\text{acac})_2$. At the same time, the solution began to develop a pink tinge. From the polarographic and coulometric data, it is concluded that the reduction process represented by wave II is, as follows



This reaction is irreversible and the reduction product dissociates in the following way,



The free acetylacetonate anion takes part in the anodic reaction associated with wave I.

3.2. Chronoamperometry

Chronoamperograms for different solutions of $\text{Co}(\text{acac})_3$ were recorded over the whole potential range of wave II, i.e., -0.86 to 1.1 V.

Current (i_t) versus (time) $^{-1/2}$ plots were straight lines: the resulting data are shown in table 1.

The linear plots of i_t against $t^{-1/2}$ provide further evidence that the electro-

Table 1. Diffusion coefficient of $\text{Co}(\text{acac})_3$ in propylene carbonate (0.1 M NaClO_4 ; 0.008% TRX-100, $T = 25^\circ \text{C}$).

Concentration (mM)	Slope of i_c vs $t^{-1/2}$ (amp sec $^{-1}$) $\times 10^{-7}$	Diffusion Coefficient (D) (cm 2 sec $^{-1}$) $\times 10^{-7}$
1. 0.22	4.89	5.14
2. 0.20	4.42	5.08
3. 0.21	4.72	5.05
Average 5.09 ± 0.05		

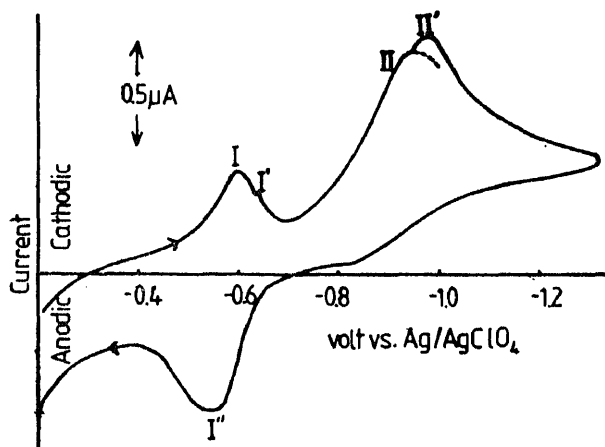


Figure 2. Cyclic voltammogram of $\text{Co}(\text{acac})_3$ (0.50 mM) in propylene carbonate with 0.1 M NaClO_4 and 0.008% TRX-100 ($V = 0.02 \text{ V/s}$; $T = 25^\circ \text{C}$).

Cyclic voltammetry

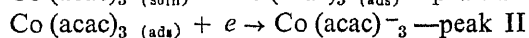
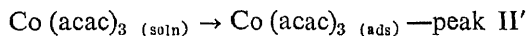
Cyclic voltammogram for $\text{Co}(\text{acac})_3$ is shown in figure 2. Peaks I' and I'' were found to show the characteristics of adsorption waves. At low concentrations ($< 0.2 \text{ mM}$) and low scan rates, they appear as sharp, separate peaks. At higher concentrations, I' appears as a shoulder which merges with an enlarged peak I in subsequent cycles. Peak II', however, merges with peak II in the first scan and separates as a shoulder in subsequent scans. At high scan rates, it again merges with peak II. Peak II is diffusion-controlled and corresponds to the diffusion-controlled wave found in polarography. The peak height is usually distorted by the presence of peak II', which is presumably due to the adsorption of reactant molecules (Wopschall and Shain 1967). On the anodic sweep, there is no peak corresponding to peak II indicating the irreversibility of the electrode reaction in agreement with the polarographic results. The anodic peak I'' was found to increase on addition of the ligand as sodium

Current flow ceases when a limiting thickness is attained and, at slow scan rates, a limiting thickness appears to be attained at all concentrations studied. At high scan rates, (e.g., 0.5 V/sec), concentrations above 0.6 mM produce limiting thickness.

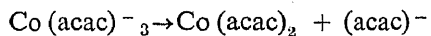
The cathodic peak I appears to be symmetrical with a slight shoulder, I', which smoothed out at high scan rates and concentrations. The peak current, very small on the initial scan becomes larger with subsequent scans with the peak potential shifting towards a more negative potential and engulfing peak I'. Peak I is therefore, attributed to the stripping of the deposition product from the electrode.

Detailed investigation of the diffusion controlled peak II was not possible due to the distortion caused by the proximity of peak II'.

In summary, the mechanism on the basis of cyclic voltammetry which is in agreement with the polarographic results, appears to be as follows :



The reverse process is negligible as the reaction is irreversible. Co (acac)_3^- is released into solution and dissociates in the following way



In the presence of (acac) ions, mercury is oxidized ultimately producing Hg (acac)_2 . Peak I'' is due to the deposition of Hg (acac)_2 until a limiting thickness is attained. Peak I is caused by the stripping of the deposit. Peak I' which was shown to be an absorption wave may be due to re-absorption of some of the stripped Hg (acac)_2 .

Electrochemical investigations in DMSO

Cyclic voltammograms of Co (acac)_3 in DMSO under the same conditions as for propylene carbonate showed reduction wave at $E_{1/2} = -0.650$ V. The pre-wave found in propylene carbonate, however, was absent (figure 3). It is interesting to consider the apparent solvent dependency of this pre-wave. It will be recalled that the pre-wave in propylene carbonate occurred at $E_{1/2} = -0.497$ V which is on the descending position of the first electrocapillary maximum as shown on the electrocapillary curve (figure 4a). It was proposed that this pre-wave is due to the adsorption of a first layer of the product Hg (acac)_2 on the electrode. Now the descending parts of an electrocapillary maximum refers to a negatively-charged mercury drop (Kolthoff and Lingane 1952). It would appear, therefore, that adsorption is reasonable in this region due to the electropositive nature of the mercuric complex. For an adsorption pre-wave to occur in DMSO, it would have to be at a potential less negative than -0.65 V, the half-wave potential. However, as shown in the electrocapillary curve for Co (acac)_3 in DMSO (figure 4b) this would be on the ascending part of the curve, where the mercury drop has a positive charge (Kolthoff and Lingane 1952). Conditions would not, therefore, be favourable for the adsorption of the mercuric complex onto the electrode.

Cyclic voltammograms of Co (acac)_3 in DMSO under the same conditions as for propylene carbonate were, apart from the absence of additional adsorption

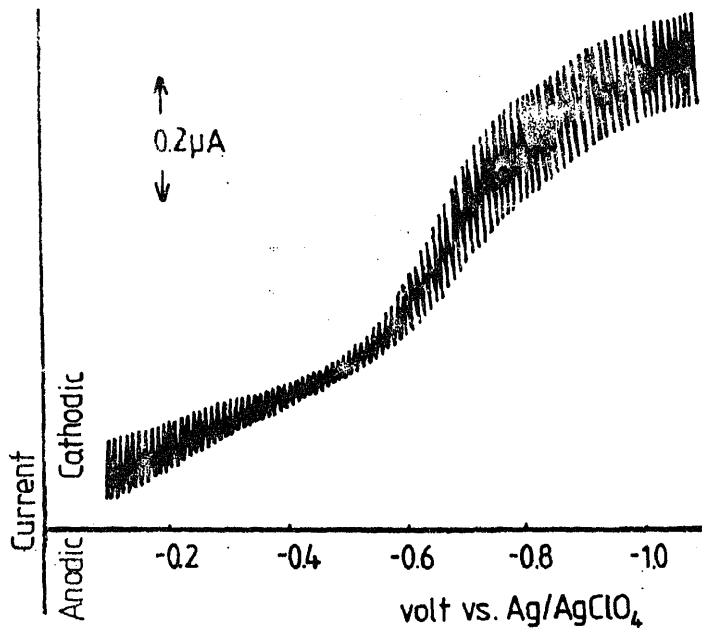


Figure 3. Polarogram of $\text{Co}(\text{acac})_3$ (0.53 mM) in DMSO with 0.1 M NaClO_4 and 0.008% TRX-100 ($T = 25^\circ\text{C}$; Hg height = 67.5 cm).

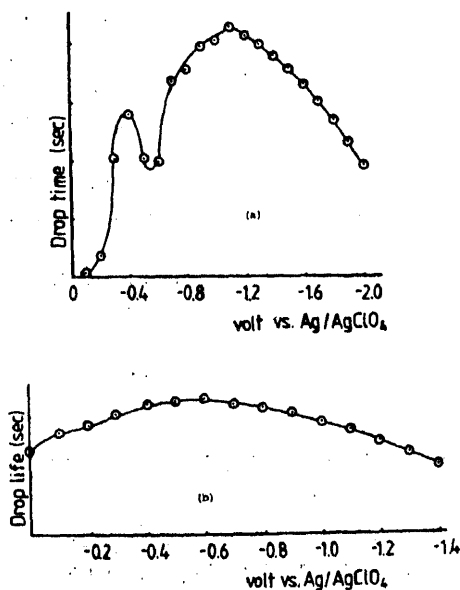
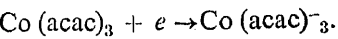


Figure 4. Electrocapillary curves of $\text{Co}(\text{acac})_3$ (1.00 mM) (a) in propylene carbonate, (b) in DMSO with 0.1 M NaClO_4 and 0.008% TRX-100.



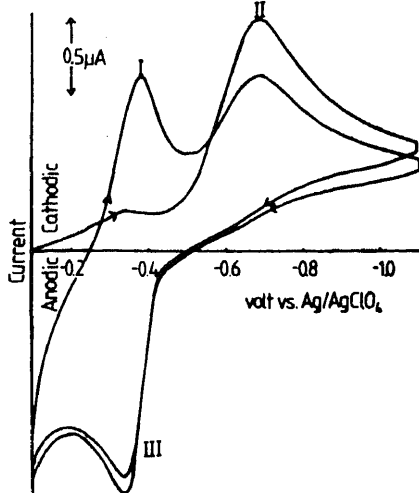


Figure 5. Cyclic voltammogram of $\text{Co}(\text{acac})_3$ (0.53 mM) in DMSO with 0.1 M NaClO_4 and 0.008% TRX-100 ($V = 0.1 \text{ V/s}$; $T = 25^\circ \text{C}$).

rate which is in accord with diagnostic criteria for an irreversible charge transfer (Brown and Lange 1971). As expected for an irreversible process; there is no corresponding peak to peak II on the anodic sweep.

Anodic peak III represents deposition of $\text{Hg}(\text{acac})_2$ onto the electrode, until a limiting thickness is achieved. The presence of $\text{Hg}(\text{acac})_2$ was confirmed by exhaustive electrolysis, which resulted in the formation of a greyish precipitate and a pink coloration in the solution. Microanalysis and IR spectroscopy confirmed the grey precipitate as $\text{Hg}(\text{acac})_2$.

Peak I is due to the stripping of the deposition from the cathode. It was found that on the initial scan, when no deposit is present, no stripping current is present (figure 5).

In other respects, the mechanism of reduction in DMSO is identical to that in propylene carbonate.

References

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Spectrophotometric studies on the formation of adducts involved in extraction of U(VI) by mixtures of HTTA with some neutral extractants

V V RAMAKRISHNA, R SWARUP and S K PATIL*

Radiochemistry Division, Bhabha Atomic Research Centre, Trombay,
Bombay 400 085, India

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Abstract. The adduct formation of $\text{UO}_2(\text{TTA})_2$ with the neutral donors TBP, DBBP and TOPO, in benzene, was investigated spectrophotometrically and it was found that each of these donors form a 1 : 1 adduct with $\text{UO}_2(\text{TTA})_2$. It was also shown spectrophotometrically that the adduct $\text{UO}_2(\text{TTA})_2 \cdot \text{S}$ can also be formed, in the organic medium according to the equilibrium, $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{S} + 2\text{HTTA} + \text{S} \rightleftharpoons \text{UO}_2(\text{TTA})_2 \cdot \text{S} + 2(\text{HNO}_3 \cdot \text{S})$

Keywords. Solvent extraction ; synergism ; $\text{UO}_2(\text{TTA})_2$ -neutral donor adducts.

Introduction

Synergic solvent extraction of U(VI) by mixtures of thenoyltrifluoroacetone (HTTA) in combination with various neutral extractants (S) was studied by several workers. It was inferred that the adduct formation responsible for the observed synergism occurs in the organic phase and the composition of the adducts and their formation constants were estimated from the extraction data. No work, however, was reported on such adduct formation studies, directly in organic media. The adduct formation between copper chelates and neutral donors (Grannon and Watton 1961 ; Walker and Li 1965 ; Dyrssen and Petkovic 1965) between U(IV) (Ramakrishna *et al* 1980 ; Patil *et al* 1979 ; Patil and Ramakrishna 1979), Np (IV) (Patil *et al* 1981a) and Pu(IV) (Ramakrishna *et al* 1979 ; Patil *et al* 1980b ; Patil *et al* 1981d) chelates and neutral donors, in organic media, has been successfully demonstrated by using spectrophotometric methods. In the present work the adduct formation between $\text{UO}_2(\text{TTA})_2$ and the neutral donors tri-*n*-butyl-phosphate (TBP), di-*n*-butyl-*n*-butylphosphonate (DBBP) and tri-*n*-butyl phosphine oxide (TOPO), in benzene, was investigated spectrophotometrically and the results are reported here.

In the extraction of U(VI) by mixtures of HTTA and TBP, from nitric acid medium, it was reported (Irving and Edgington 1960) that the observed syner-

therefore, felt interesting to study the nature of the equilibrium between $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ and $\text{UO}_2(\text{TTA})_2 \cdot \text{TBP}$ in the organic phase and see whether any mixed NO_3 —TTA adduct is formed. Such systems involving the donors TBP and DBBP were investigated spectrophotometrically and the results are included here.

2. Experimental

2.1. Materials

Analar grade uranyl nitrate hexahydrate was obtained from M/s BDH Chemicals Ltd., England. TBP was obtained from M/s Monsanto chemicals USA, and was purified (Alcock *et al* 1956). DBBP was obtained from M/s K and K labs USA and was purified (Healy *et al* 1977). TOPO and HTTA (M/s E. Merck, West Germany) were kept under vacuum, for a few hours, before use.

The compound $\text{UO}_2(\text{TTA})_2$ was prepared (Prasad 1963) by mixing alcoholic solutions of uranyl nitrate and HTTA, the former slightly in excess over the stoichiometric ratio, and then precipitating $\text{UO}_2(\text{TTA})_2$ by addition of excess water. The precipitate was washed thoroughly with alcohol-water mixture and vacuum dried, in a desiccator, over P_2O_5 . The m.p. (212°C) and DTA curve of the compound were in agreement with the reported (Prasad 1963) data. Stock solutions of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{DBBP}$ in benzene were prepared by equilibrating 0.10 M TBP in benzene and 0.10 M DBBP in benzene respectively, with solid uranyl nitrate hexahydrate. The solutions were analysed for their uranium concentration which was found to be 0.05 M in each case and this is in agreement with the formulae given. Benzene solutions of $\text{TBP} \cdot \text{HNO}_3$ and $\text{DBBP} \cdot \text{HNO}_3$ were prepared by equilibrating the donors with required quantities of conc. nitric acid. All other chemicals used were of Analar grade.

2.2. Procedure

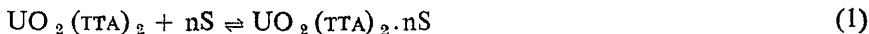
For studying the equilibria between $\text{UO}_2(\text{TTA})_2$ and the neutral donors (S) several solutions of a fixed concentration of $\text{UO}_2(\text{TTA})_2$ with varying concentrations of neutral donor under investigation were prepared. The absorption spectra of these solutions were recorded, in the visible region, using Cary—14 recording spectrophotometer employing 10 cm path length cells. The neutral donors, at the concentrations used, were not found to absorb, in the wavelength region studied.

For studying the equilibria involving $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{S}$, several solutions $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{S}$ with varying concentrations of HTTA and S were made and their absorption at a few fixed wavelengths was recorded. The same equilibria were also studied by following the absorption of a number of solutions of $\text{UO}_2(\text{TTA})_2$ containing different amounts of S and $\text{S} \cdot \text{HNO}_3$.

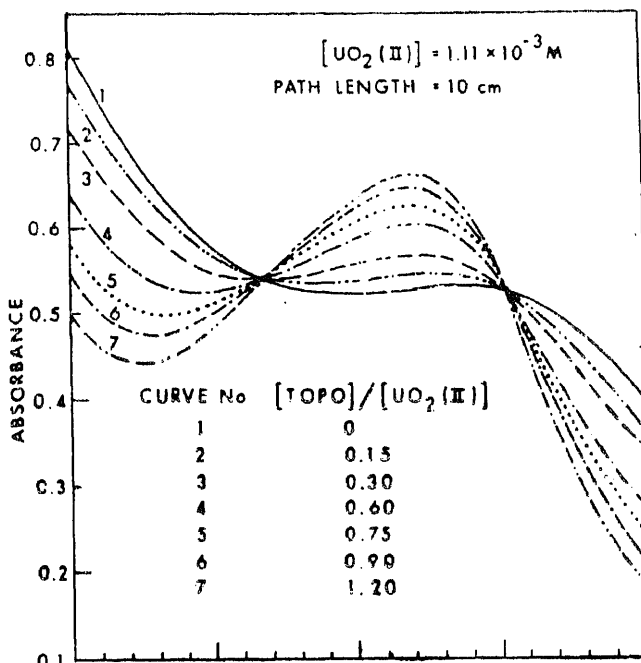
3. Results

3.1. Adduct formation between $\text{UO}_2(\text{TTA})_2$ and S

The formation of adducts between $\text{UO}_2(\text{TTA})_2$ and a neutral donor S can be represented as



The absorption spectrum of $\text{UO}_2(\text{TTA})_2$ and the changes caused to it by addition of different amounts of TOPO (figure 1) showed the presence of isosbestic points suggesting that there are only two absorbing species present in the system viz., $\text{UO}_2(\text{TTA})_2$ and an adduct of it with TOPO. The plots of the change in absorbance, at fixed wavelengths, with $[\text{TOPO}]/[\text{U(VI)}]$ (figure 2) showed that the absorption data correspond with the formation of a 1:1 adduct between $\text{UO}_2(\text{TTA})_2$ and TOPO. The spectral data did not give any indication regarding the formation of any higher adducts though the formation of $\text{UO}_2(\text{TTA})_2 \cdot 2 \text{ TOPO}$ (Healy 1961a) or $\text{UO}_2(\text{TTA})_2 \cdot 3 \text{ TOPO}$ (Healy 1961b) were reported from extraction studies and that of $\text{UO}_2(\text{TTA})_2 \cdot 3 \text{ TOPO}$ was reported (Ferraro and Healy 1962) from structural studies. Similar spectral data obtained with DBBP and TBP showed that the adducts formed are, respectively, $\text{UO}_2(\text{TTA})_2 \cdot \text{DBBP}$ and $\text{UO}_2(\text{TTA})_2 \cdot \text{TBP}$.



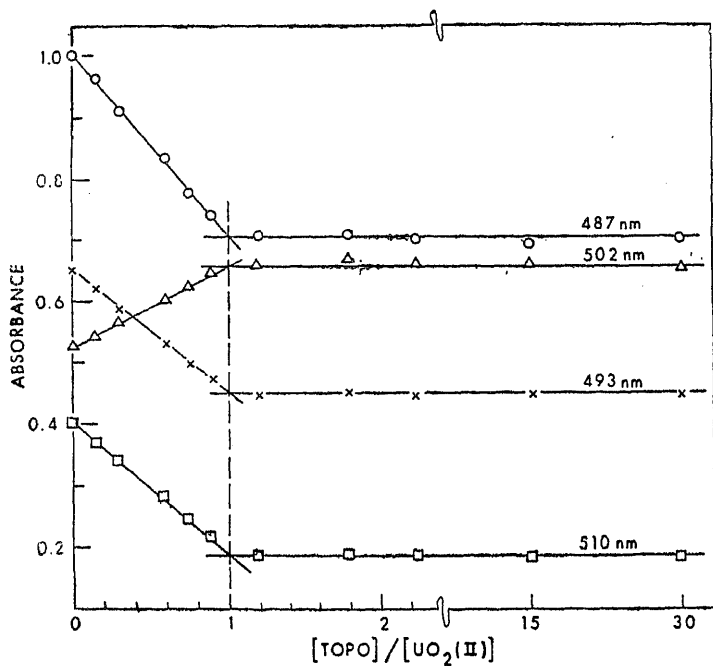
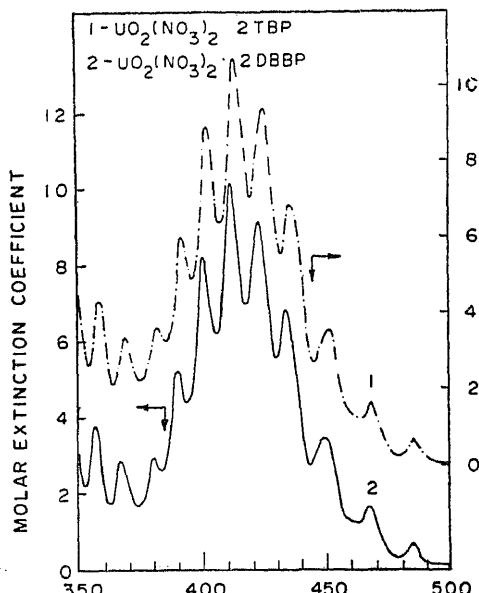
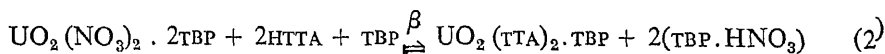


Figure 2. Variation of the absorbance value of U(VI) with $[TOPO]/[U(VI)]$.



2. Equilibria involving $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{S}$ and $\text{UO}_2(\text{TTA})_2 \cdot \text{S}$

The absorption spectra of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{DBBP}$, in benzene are shown in figure 3. The spectra are identical to one another and their molar extinction coefficient values, in the wavelength region shown, are much lower as compared to those observed for $\text{UO}_2(\text{TTA})_2$ or $\text{UO}_2(\text{TTA})_2 \cdot \text{S}$. When different amounts of HTTA were added to a solution of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$, in presence of excess but constant (TBP), the extinction coefficient values continuously increased finally reaching a constant. The latter constant value was the same as that of $\text{UO}_2(\text{TTA})_2 \cdot \text{TBP}$, observed earlier, thereby indicating complete conversion of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ to $\text{UO}_2(\text{TTA})_2 \cdot \text{TBP}$. From the data obtained (table 1) the constant β for the equilibrium represented by equation



was calculated as given below.

The equilibrium constant β is given by

$$\beta = [\text{UO}_2(\text{TTA})_2 \cdot \text{TBP}] [\text{TBP} \cdot \text{HNO}_3]^2 / [\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}] [\text{HTTA}_2]^2 [\text{TBP}] \quad (3)$$

when a given absorption spectrum is due to a mixture of two absorbing species the observed molar extinction coefficient, E , at a particular wavelength, can be given by the relation,

$$EC = E_1 C_1 + E_2 C_2 \quad (4)$$

In the present case, the total concentrations (C) of the absorbing uranyl ion is given by

$$C = C_1 + C_2 \quad (5)$$

Table 1. Spectrophotometric data concerning the equilibrium, $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP} + 2\text{HTTA} + \text{TBP} \xrightleftharpoons{\beta} \text{UO}_2(\text{TTA})_2 \cdot \text{TBP} + 2(\text{TBP} \cdot \text{HNO}_3)$

$$[\text{U(VI)}] = 6.3 \times 10^{-4} \text{ M.}$$

[TBP] M $\times 10$	[HTTA] M $\times 10^3$	E at, (nm)			β at, (nm)		
		430	440	450	430	440	450
0.101	6.24	881	560	400	0.31	0.31	0.29
0.101	3.12	590	373	270	0.26	0.26	0.26
0.198	3.12	643	421	314	0.35	0.22	0.25
0.0513	6.24	714	437	302	0.24	0.20	0.18

the observed E values it can be shown from (4) and (5) that

$$C_1 = C(E_2 - E)/(E_2 - E_1) \quad (6)$$

$$\text{and } C_2 = C(E - E_1)/(E_2 - E_1) \quad (7)$$

If one denotes the total concentrations of TBP, HTTA and $\text{TBP} \cdot \text{HNO}_3$ respectively as a , b and d and their equilibrium concentrations respectively as a_1 , b_1 and d_1 , it follows from (2) that,

$$a_1 = a - c_2 - 2C_1 \quad (8)$$

$$b_1 = b - 2C_2 \quad (9)$$

$$\text{and } d_1 = d - 2C_2 \quad (10)$$

The equilibrium constant β , represented by (3) can now be rewritten as

$$\beta = c_2 \cdot d_1^2 / c_1 \cdot b_1^2 \cdot a_1 \quad (11)$$

The values of β , thus obtained using the data, at different wavelengths, and at different concentrations of TBP and HTTA are included in table 1. From these an average value of $\beta = 0.26 \pm 0.05$ was obtained for equation (2).

The equilibrium represented by (2) was also studied in reverse by the addition of different amounts of $\text{TBP} \cdot \text{HNO}_3$ to a solution of $\text{UO}_2(\text{TTA})_2$ in excess TBP and recording the spectral changes. The data obtained are given in table 2 and from these data the equilibrium constant $\beta^* (= 1/\beta)$ was calculated and the values of β^* are also included in table 2, the average value being $\beta^* = 3.1 \pm 0.5$. The value of d_1 for these calculations is given by,

$$d_1 = d - 2C_1 \quad (12)$$

Table 2. Spectrophotometric data concerning the equilibrium, $\text{UO}_2(\text{TTA})_2 \cdot \text{TBP} + 2(\text{TBP} \cdot \text{HNO}_3) \rightleftharpoons \text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP} + 2\text{HTTA} + \text{TBP}$.

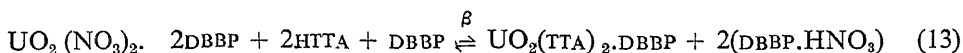
$$[\text{U(VI)}] = 5.79 \times 10^{-4} \text{ M}, [\text{TBP} \cdot \text{HNO}_3] = 1.844 \times 10^{-3} \text{ M}.$$

[TTP] $\text{M} \times 10^2$	[HTTA] $\text{M} \times 10^3$	E at, (nm)			$\beta^* = 1/\beta$ at, (nm)		
		430	440	450	430	440	450
1.50	7.56	320	192	117	2.8	3.2	4.3
1.50	14.0	583	364	244	2.7	2.8	3.4
2.75	7.56	451	278	183	2.8	2.9	3.6
1.38	7.56	825	520	356	2.5	2.2	3.6
2.75 ^a	14.0	730	456	307	2.8	2.9	3.6
	E_1	6	5	3			
	E_2	1446	915	665			

(^a) $(\text{TBP} \cdot \text{HNO}_3) = 9.22 \times 10^{-4} \text{ M}$.

It can be seen that the values of β obtained by approaching the equilibrium, represented by (2), either way are in good agreement with one another.

Similar results obtained in the study of the equilibrium



are given in table 3, for which an average value of $\beta = 0.48 \pm 0.05$ was obtained. This equilibrium was also confirmed by approaching it in a reverse way as described above for TBP.

4. Discussion

This study, thus supports the conclusion arrived at from solvent extraction work that synergism in the extraction of U(VI) by mixtures of HTTA and a neutral donor is due to the formation of an adduct between the metal chelate and the neutral donor, in the organic phase. Besides, it is established that there exists an equilibrium between the synergic adduct and the neutral donor complex of the metal salt, which, in fact, decides the extent of synergism when metal ion is extracted from an aqueous medium from which the neutral donor alone is able to extract the metal ion. The present study did not reveal the presence of and mixed adduct such as $\text{UO}_2(\text{NO}_3)(\text{TTA}) \cdot \text{TBP}$ and, thus, is in agreement with the recent extraction studies (Patil *et al* 1981c). The absence of such a mixed adduct in these systems is surprising since a number of such mixed $\text{NO}_3\text{-TTA-S}$ adducts were shown to be formed in the extraction of trivalent lanthanides (Cox and Davis 1973 ; Cunninghame *et al* 1954 ; Gerow *et al* 1977 ; Hayden *et al* 1974 ; Irving and Edgington 1961b) as well as trivalent (Cox and Davis 1973 ; Irving and Edgington 1961b ; Ramanujam *et al* 1981) and tetravalent (Irving and Edgington 1961a ; Patil *et al* 1980c ; Patil *et al* 1981b) actinides from nitrate media. Thus the lack of formation of such a mixed adduct by uranyl ion can probably be ascribed only to limitations due to structural factors. Recent

Table 3. Spectrophotometric data concerning the equilibrium, $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{DBBP} + 2\text{HTTA} + \text{DBBP} \xrightleftharpoons{\beta} \text{UO}_2(\text{TTA})_2 \cdot \text{DBBP} + 2(\text{DBBP} \cdot \text{HNO}_3)$.
 $[\text{U(VI)}] = 6.25 \times 10^{-4} \text{ M}$

[DBBP] M	[HTTA] $\text{M} \times 10^3$	E at, (nm)			β at, (nm)		
		420	430	440	420	430	440
0.101	0.625	322	216	144	0.44	0.48	0.55
0.101	1.25	510	344	226	0.43	0.47	0.52
0.101	1.56	590	396	260	0.43	0.47	0.51
0.101	3.13	876	592	384	0.38	0.43	0.46
0.0513	3.13	768	512	332	0.56	0.47	0.50
0.0263	3.13	644	436	280	0.45	0.50	0.51
	E_1	7	6	6			

work on synergistic extraction of Np(VI) (Patil et al. 1980a) has also shown that $\text{NpO}_2(\text{NO}_3)$ (TTA). TBP is not involved in the extraction. It would be interesting to know what factors prevent the formation of such mixed species in case of hexavalent actinides and much work is needed to throw light on this aspect.

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Syntheses and characterisation of ruthenium carbonyl clusters containing phosphorus and arsenic bridging ligands

K NATARAJAN* and G HUTTNER†

Department of Chemistry, Bharathiar University, Coimbatore 641 046, India

†Fakultät für Chemie der Universität Konstanz, D 7750 Konstanz W. Germany

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Abstract. Ruthenium carbonyl clusters, $[\text{Ru}_3(\text{CO})_9(\mu_3\text{-AsC}_6\text{H}_5)_2]$, $[\text{Ru}_4(\text{CO})_{13}(\mu_3\text{-AsC}_6\text{H}_5)_2]$ and $[\text{Ru}_3(\text{CO})_9(\mu_3\text{-P}(\text{C}_6\text{H}_5)_2)_2]$ have been synthesised and characterised by elemental analysis, NMR (^1H and ^{31}P), mass and infrared spectral measurements. Structures have been proposed on the basis of the spectroscopic data.

Keywords. Ruthenium carbonyl cluster; phosphorus and arsenic ligands.

1. Introduction

Considerable amount of work has been done on homo and heterometallic carbonyl clusters containing $\mu_3\text{-PR}$ bridged ligands (Huttner *et al* 1976b, c, 1978a, b; De 1979). Comparatively very little attention has been paid to the analogous $\mu_3\text{-AsR}$ bridged clusters and only a few are reported Huttner *et al* 1976a; Rottinger and Vahrenkamp 1978; Schneider and (Huttner 1981; Natarajan *et al* 1981). Our interest in the reactivity of clusters stabilised by bridging or capping arsenic ligands (Natarajan *et al* 1981) has led us to attempt the preparation of ruthenium chromium heterometallic cluster from $[(\text{CO})_5\text{CrAs}(\text{C}_6\text{H}_5)_2\text{H}_2]$ and $\text{Ru}_3(\text{CO})_{12}$. The reactions of primary phosphines PRH_2 (R = alkyl or aryl) with $\text{M}_3(\text{CO})_{12}$ (M = Fe, Ru) (Huttner *et al* 1980; Natarajan *et al* 1981) yielded $[(\mu_3\text{-H})_2\text{M}_3(\text{CO})_9(\mu_3\text{-PR})]$ and $[(\mu_3\text{-H})_2\text{M}_3(\text{CO})_9(\mu_3\text{-PR})_2]$ whereas with osmium, the mono-substituted $[\text{Os}_3(\text{CO})_{11}(\text{PRH}_2)]$ and edge bridged $[(\mu_2\text{-H})\text{Os}_3(\text{CO})_{10}(\mu_2\text{-PRH})]$ have been obtained (Natarajan *et al* 1981a). It is quite possible that the reactions of PRH_2 with $\text{M}_3(\text{CO})_{12}$ (M = Fe, Ru) also occur with initial substitution of a CO group in $\text{M}_3(\text{CO})_{12}$ by primary phosphines leading to $[\text{M}_3(\text{CO})_{11}(\text{PRH}_2)]$, with subsequent migration and CO substitution process, resulting in $[(\mu_2\text{-H})\text{M}_3(\text{CO})_{10}(\mu_2\text{-PRH})]$ and $[(\mu_2\text{-H})_2\text{M}_3(\text{CO})_9(\mu_3\text{-PR})]$. Though we have been unsuccessful in obtaining the intermediates in our attempts, a recent paper (Iwasaki *et al* 1981) describes the isolation of the intermediate

* To whom all correspondence should be made

2. Experimental

2.1. Materials and characterisation

Dodecacarbonyltriruthenium (Bruce and Stone 1967) and $[(\text{CO})_5\text{CrAs}(\text{C}_6\text{H}_5)_2]$ (Strohmeier 1964) were prepared according to the published methods. $\text{P}(\text{C}_6\text{H}_5)_3$ was obtained from Strem chemical corporation. The solvents used were dried over sodium-benzophenone and distilled under nitrogen. All operations were performed either under oxygen free nitrogen or under vacuum. Microanalyses were done at the Microanalytical section of the Department of Chemistry, University of Constance, W. Germany. Infrared spectra were obtained on a Zeiss spectrometer IMR-40 and NMR (^{31}P and ^1H) were recorded on Bruker WP-FT spectrometer. Mass spectra were obtained with a Varian MAT 312 spectrometer at 70 eV. Melting points were determined in open capillaries using Gallenkamp melting point apparatus and are uncorrected.

2.2. Preparations

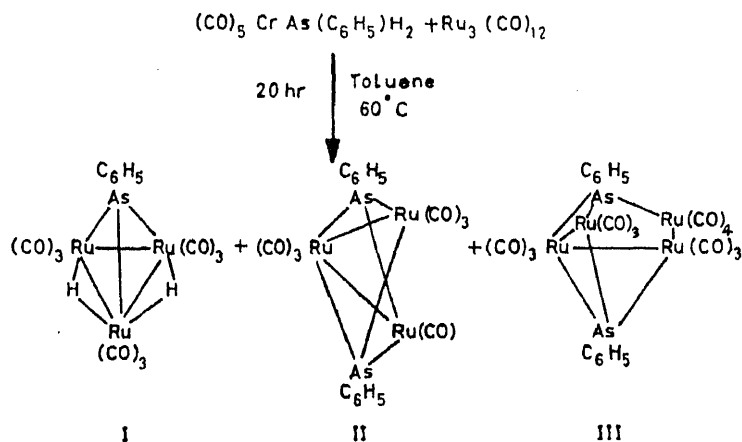
2.2a. Reaction of $[(\text{CO})_5\text{CrAs}(\text{C}_6\text{H}_5)_2\text{H}_2]$ with $\text{Ru}_3(\text{CO})_{12}$: To a suspension of $\text{Ru}_3(\text{CO})_{12}$ (320 mg, 0.5 mmol) in toluene (60 cm³) was added $[(\text{CO})_5\text{CrAs}(\text{C}_6\text{H}_5)_2\text{H}_2]$ (173 mg, 0.5 mmol) and stirred at 60° C for 20 hr. The solvent was evaporated under vacuum to a small volume (5 cm³) and silica gel (5 g) was added to it. The residue was then dried under vacuum and transferred to a silica gel column made up of pentane at -30° C. The first, yellow fraction, eluted with pentane gave $\text{Ru}_3(\text{CO})_{12}$. The second, yellow fraction eluted with 10/1 pentane/toluene, gave $[(\mu_2\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-AsC}_6\text{H}_5)_2]$ (45 mg, 12.6% based on $\text{Ru}_3(\text{CO})_{12}$). The third, red fraction, eluted with 2/1 pentane/toluene, gave $[\text{Ru}_3(\text{CO})_9(\mu_3\text{-AsC}_6\text{H}_5)_2]$ (38 mg, 8.8% based on $\text{Ru}_3(\text{CO})_{12}$). The fourth, red fraction eluted with 1/1 pentane/toluene gave $[\text{Ru}_4(\text{CO})_{13}(\mu_3\text{-AsC}_6\text{H}_5)_2]$ (26 mg, 5% based on $\text{Ru}_3(\text{CO})_{12}$). $[\text{Ru}_3(\text{CO})_9(\mu_3\text{-AsC}_6\text{H}_5)_2]$ m.p. 140-44° C (d). Mass spec. m/e 859. Anal. Calcd. for $\text{C}_{21}\text{H}_{10}\text{O}_9\text{As}_2\text{Ru}$: C, 29.33; H, 1.16; As, 17.46. Found: C, 29.76; H, 1.12; As, 17.82. IR (toluene): 2115 (s); 2083 (s); 2058 (s); 2019 (m); 1997 (w); 1926 (s) cm⁻¹. $^1\text{H-NMR}$ (Acetone- d_6): 7.55 (m) ppm. $[\text{Ru}_4(\text{CO})_{13}(\mu_3\text{-AsC}_6\text{H}_5)_2]$: m.p. 165-170° C (d). Mass spec. m/e 1072. Anal. Calcd. for $\text{C}_{25}\text{H}_{10}\text{O}_{13}\text{As}_2\text{Ru}$: C, 27.98; H, 0.93; As, 13.99. Found: C, 28.10; H, 0.88, As, 14.21. IR (toluene): 2140 (w); 2070 (s); 2054 (s); 2035 (m); 2025 (w); 2015 (w); 1937 (m); 1983 (w). $^1\text{H-NMR}$ (acetone- d_6): 7.32 (m) ppm.

2.2b. Reaction of $\text{P}(\text{C}_6\text{H}_5)_2\text{H}$ with $\text{Ru}_3(\text{CO})_{12}$: To a suspension of $\text{Ru}_3(\text{CO})_{12}$ (320 mg, 0.5 mmol) in toluene (60 cm³) was added $\text{P}(\text{C}_6\text{H}_5)_2\text{H}$ (93 mg, 0.5 mmol) and stirred at 60° C for 12 hr. The product, after work up as given

$\text{Ru}_3(\text{CO})_{12}$: m.p. 140–45°C (d) mass. spec. m/e 740. Anal. calcd. for $\text{I}_{20}\text{O}_6\text{P}_2\text{Ru}_2$: C, 48.65; H, 2.70; P, 8.38. Found: C, 48.96; H, 2; P, 8.38. IR (toluene): 2078 (s); 2044 (s); 2027 (s); 1985 (m); 1971 (w). ^{31}P NMR (toluene): 163.1 (s) ppm. ^1H -NMR (acetone- d_6): 7.55 (m) ppm.

Results and discussion

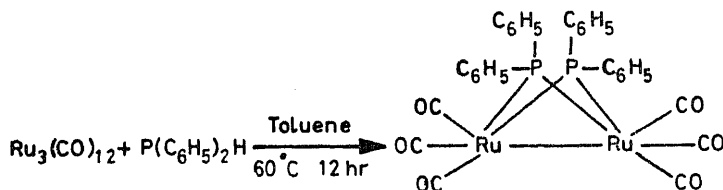
of the methods for the synthesis of heterometallic phosphorus-bridged clusters involves in dehalogenation of dichlorophosphine complexes by iron carbonyl, $(\text{CO})_{12}$ (Huttner *et al* 1976b, c, 1978a, b; De 1979). However, $\text{Ru}_3(\text{CO})_{12}$ did function like $\text{Fe}_3(\text{CO})_{12}$ and yielded only homometallic clusters of the type $(\text{CO})_{15}(\mu_4\text{-PR})$ (Natarajan *et al* 1981b). But, $[(\text{C}_6\text{H}_5)(\text{CO})_2\text{MnPRH}_2]$ reacts with $\text{Ru}_3(\text{CO})_{12}$ to give the expected heterometallic cluster $(\text{RPMnRu}_2)_8(\text{C}_6\text{H}_5)$ (Schneider and Huttner 1981). In the present study, we extended this method in order to obtain the corresponding arsenic bridged heterometallic cluster. Surprisingly, from the reaction of $[(\text{CO})_5\text{CrAs}(\text{C}_6\text{H}_5)_2]$ with $(\text{CO})_{12}$, we did not obtain the expected heteronuclear cluster of the type, $(\text{H}_5\text{AsCrRu}_2)(\text{CO})_{11}$ but isolated chromium free $[(\mu_3\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-AsI}_6)]$, $[\text{Ru}_3(\text{CO})_9(\mu_3\text{-AsC}_6\text{H}_5)_2]$ and $(\text{Ru}_4(\text{CO})_{13}(\mu_3\text{-AsC}_6\text{H}_5)_2]$. The fate of the chromium fragment is not clear at present, nor is the role played by chromium in this reaction



The compound $[(\mu_3\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-AsC}_6\text{H}_5)]$ (I) has already been reported (Natarajan *et al* 1981). Mass spectroscopic and analytical data indicate that the cluster II has the composition $[\text{Ru}_3(\text{CO})_9(\text{AsC}_6\text{H}_5)_2]$. The molecular peak in the mass spectrum for this compound was quite apparent and fragmentation by successive loss up to 9 carbonyl groups has been observed. IR spectrum is very similar to the one observed for the analogous $(\text{Fe}_3(\text{CO})_9(\mu_3\text{-AsC}_6\text{H}_5)_2]$ (Huttner *et al* 1976a) indicating a similar structure. In the ^1H -NMR spectrum, a multiplet around 7.55 ppm shows the presence of phenyl groups. Based on the spectro-

scopic data and in comparison with the known crystal structure of $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-AsC}_6\text{H}_5)_2]$, structure II has been proposed.

Along with compounds I and II, a third compound $[\text{Ru}_4(\text{CO})_{13}(\mu_3\text{-AsC}_6\text{H}_5)_2]$ (III) has also been obtained from the reaction of $[(\text{CO})_5\text{CrAs}(\text{C}_6\text{H}_5)_2\text{H}_2]$ with $\text{Ru}_3(\text{CO})_{12}$. Analytical and mass spectroscopic data confirm the molecular formula $[\text{Ru}_4(\text{CO})_{13}(\text{AsC}_6\text{H}_5)_2]$. Non equivalent nature of the carbonyl groups is apparent from the more number of infrared bands observed in the ν_{CO} region (refer experimental section). The presence of phenyl groups is inferred from the ^1H -NMR spectrum of this compound which shows a resonance at 7.32 (m) ppm. The crystal and molecular structure has been determined by single crystal x-ray diffraction technique (Natarajan *et al* 1982) which is as shown in III.



The reaction of $\text{P}(\text{C}_6\text{H}_5)_2\text{H}$ with $\text{Ru}_3(\text{CO})_{12}$ yielded $[\text{Ru}_2(\text{CO})_6(\mu_2\text{-P}(\text{C}_6\text{H}_5)_2)_2]$. The pattern of $\nu_{(\text{CO})}$ bands observed in the infrared spectrum of this compound is close to that observed for the analogous compounds $[\text{Fe}_2(\text{CO})_6(\text{PRH})_2]$ (Treichel *et al* 1972), $[\text{Ru}_2(\text{CO})_6(\text{AsMe}_2)_2]$ (Roland and Vahrenkamp 1980) and $[\text{Ru}_2(\text{CO})_6(\text{As}(\text{C}_6\text{H}_5)_2)_2]$ (Natarajan *et al* 1981) which shows that the framework geometry is similar to the one found for these compounds with a nonplanar Ru_2P_2 cycle. Its ^{31}P -NMR spectrum shows a singlet at 163.1 ppm which indicates chemically equivalent bridging phosphorus ligands. In the ^1H -NMR spectrum a multiplet at 7.55 ppm indicates the phenyl groups.

The reaction of $\text{P}(\text{C}_6\text{H}_5)_2\text{H}$ with $\text{Ru}_3(\text{CO})_{12}$ has been carried out with the view to obtaining edge bridged hybrid cluster $[(\mu_2\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu_2\text{-P}(\text{C}_6\text{H}_5)_2)_2]$ analogous to the osmium cluster $[(\mu_2\text{-H})\text{Os}_3(\text{CO})_{10}(\mu_2\text{-PRH})]$ (Natarajan *et al* 1981a). It is anticipated that the secondary phosphine, $\text{P}(\text{C}_6\text{H}_5)_2\text{H}$ would prevent the formation of capped cluster and would favour only the edge bridged one. However, we could only isolate a bridged dinuclear compound, $[\text{Ru}_2(\text{CO})_6(\mu_2\text{-P}(\text{C}_6\text{H}_5)_2)_2]$. It could be that the conditions necessary for the formation of edge bridged cluster will at the same time promote the rupture of M-M bond leading to the dinuclear species with subsequent formation of an additional phosphorus bridge.

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Spectral and magnetic studies of metal thiocyanate complexes with N-substituted thioureas

S B KOKATNUR† and A S R MURTY *

Department of Chemistry, Karnatak University, Dharwad 580 003, India

†B K Arts and Science College, Chikodi, India

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Abstract. The complexes of the type $ML_2(SCN)_2$ have been synthesised from $M(SCN)_2$ [$M = Co(II), Ni(II)$] and N-substituted thioureas (L) such as chlorophenyl (Cl-Ptu), tolyl (totu), methoxy phenyl (mco-ptu), nitrophenyl (NO_2 -Ptu) and bromophenyl (Br-Ptu) thioureas. All the complexes are non-electrolytes in acetone. IR spectral studies reveal that thiourea and thiocyanate are bonded to the central metal through S and N respectively. Magnetic susceptibility studies at room temperature ($25^\circ C$) and electronic spectral data confer octahedral symmetry to nickel (II) and tetrahedral symmetry to cobalt (II) complexes.

Keywords. Spectral ; magnetic ; nickel (II) ; cobalt (II) ; N-substituted thioureas.

1. Introduction

The replacement of halides by potentially ambidentate thiocyanate groups offers interesting bonding possibilities in metal complexes. The linear thiocyanate anion may coordinate to metal through either nitrogen $M \leftarrow NCS$ or sulphur $M \leftarrow SCN$ or both $M \leftarrow NCS \rightarrow M$. $M \leftarrow NCS$ group is either linear or bent, while $M \leftarrow SCN$ group is always bent. The ν CS and δ NCS frequencies are different between the two isomers (Turco and Pecile 1961 ; Lewis *et al* 1961 ; Sabatini and Bertini 1960). Epps and Mazili (1972) have reported the isolation of the first octahedral complex containing both N and S bonded thiocyanate.

The synthesis and characterization of the complexes of the composition $[Ni L_2(SCN)_2]$ and $[Co L_2(SCN)_2]$ have been reported by Yagupsky *et al* (1965) and Maharana *et al* (1970). According to the above authors, both thiourea (through S) and thiocyanate (through N) are bonded to the metal. No reports are available on the synthesis and characterization of cobalt (II) or nickel (II) thiocyanate complexes with N and N, N' substituted thioureas. So it is proposed to carry out systematic studies of the above complexes.

2. Experimental

2.1. *Synthesis of ligands*

The ligands were synthesised from appropriate substituted amines, ammonium thiocyanate and hydrochloric acid utilizing published procedures (Kurzer 1958; Frank and Smith 1955).

2.2. *Synthesis of complexes*

The metal thiocyanate and the N-substituted thioureas were mixed in 1:1 ratio in hot ethanol. The mixture was refluxed for 30 min in the case of cobalt complex and was concentrated with constant stirring in the case of nickel complex. The solid thus obtained was filtered, washed with alcohol and ether and then dried in vacuum over P_2O_5 . In some cases the solid was separated by vigorous stirring with petroleum ether (60–80° C) and the same was treated as above.

2.3. *Chemical analysis*

All complexes were analysed for cobalt (oxinate method-gravimetric), nickel (dimethylglyoxime-gravimetric), nitrogen, sulphur and chlorine (Vogel 1962).

2.4. *Physical measurements*

Conductance studies of complexes in acetone medium were made utilizing Elico conductivity bridge type CM-82 provided with a dip type conductivity cell having cell constant 0.61.

Molar magnetic susceptibility of the complexes was measured at room temperature (25° C) by Gouy method against $Hg[Co(SCN)_4]$ as calibrant. It was corrected for diamagnetism from the data available in the table of pascal's constants (Mulay 1963).

The infrared spectra of ligands and complexes in KBr pellet were recorded on Perkin-Elmer model 257 spectrometer. The electronic spectra of the complexes in nujol mull were taken from Unicam 700 A instrument.

3. Results and discussion

3.1. *Physical properties*

The N-substituted thiourea complexes of cobalt (II) thiocyanate are blue to bluish green while those of nickel (II) are pale yellow to deep yellow powders. They are soluble in acetone. The elemental analysis favours 1:2 ratio for metal to ligand. (cf table 1). The molar conductance values fall into the range 4 to 38 mhos $cm^{-2} mol^{-1}$ at 25° C indicating their non electrolytic nature.

3.2. *Infrared spectra*

Table 1. Elemental analysis of complexes.

Sl. No.	Name of the complex	% Ni/Co	% N	% S
1.	[Ni (o-Cl Ptu) ₂ (NCS) ₂]	10·66 (10·70)	15·40 (15·33)	23·45 (23·56)
2.	[Ni (m-Cl Ptu) ₂ (NCS) ₂]	10·57 (10·70)	15·17 (15·33)	23·31 (23·56)
3.	[Ni (p-Cl Ptu) ₂ (NCS) ₂]	10·56 (10·70)	15·35 (15·33)	23·45 (23·56)
4.	[Ni (o-totu) ₂ (NCS) ₂]	11·20 (11·57)	16·36 (16·57)	25·39 (25·28)
5.	[Ni (m-totu) ₂ (NCS) ₂]	11·36 (11·57)	16·40 (16·57)	25·42 (25·28)
6.	[Ni (p-totu) ₂ (NCS) ₂]	11·43 (11·57)	16·38 (16·57)	25·07 (25·28)
7.	[Ni (o-m:O Ptu) ₂ (NCS) ₂]	11·04 (10·89)	15·77 (15·59)	23·96 (23·78)
8.	[Ni (m-NO ₂ Ptu) ₂ (NCS) ₂]	10·37 (10·31)	19·87 (19·69)	22·60 (22·52)
9.	[Ni (p-Br Ptu) ₂ (NCS) ₂]	9·09 (9·22)	13·39 (13·19)	19·94 (20·13)
10.	[Co (o-Cl Ptu) ₂ (NCS) ₂]	10·65 (10·78)	15·12 (15·33)	23·27 (23·39)
11.	[Co (m-Cl Ptu) ₂ (NCS) ₂]	11·05 (10·78)	15·04 (15·33)	23·40 (23·39)
12.	[Co (p-Cl Ptu) ₂ (NCS) ₂]	10·86 (10·78)	15·12 (15·33)	23·41 (23·39)
13.	[Co (o-totu) ₂ (NCS) ₂]	11·80 (11·61)	16·72 (16·56)	24·91 (25·27)
14.	[Co (m-totu) ₂ (NCS) ₂]	11·80 (11·61)	16·44 (16·56)	25·01 (25·27)
15.	[Co (p-totu) ₂ (NCS) ₂]	11·55 (11·61)	16·50 (16·56)	25·11 (25·27)
16.	[Co (o-m:O-Ptu) ₂ (NCS) ₂]	11·10 (10·92)	15·33 (15·58)	23·52 (23·77)
17.	[Co (m-NO ₂ Ptu) ₂ (NCS) ₂]	10·25 (10·35)	19·56 (19·68)	22·55 (22·52)
18.	[Co (p-Br Ptu) ₂ (NCS) ₂]	9·08 (9·25)	12·98 (13·19)	19·98 (20·12)

of central metal ion through S of the ligand (ν C = S group) but not N of NH has been established on the basis of the following observations (cf. table 2)

- (i) No marked shift in the ν NH region 3450-3000 cm^{-1} on complexation,
- (ii) Slight positive shift for a strong band ν NCN + δ NH₂ in the region 1540-1480 cm^{-1} ; (iii) A negative shift of the order 30 cm^{-1} ; with reduction in intensity in a few complexes for the band ν CS + ν CN in the region 780-700 cm^{-1} compared to free ligands and also a similar shift for the band ν CS at 600-680 cm^{-1}

Table 2. IR absorption frequencies (cm^{-1}) of ligands and complexes

complex	ν NH	ν NCN + δ NH ₂	ν CS + ν NCN		NCS	
			ν CS	ν CS	ν CS	ν CS
u (NCS) ₂	3355 mbr	1504 s	725 s	670 s	...	...
(NCS) ₂	3350 mbr	1510 mbr	723 w	665 ms	2100 s sh	805 mbr
(NCS) ₂	3240 ms	1505 mbr	717 s	660 mbr	2070 s	820 ms
tu (NCS) ₂	3394 vs	1515 msh	706 vs	625 s	...	...
(NCS) ₂	3410 ms	1515 mbr	690 ms	635 vw	2150 ms	720 ms
(NCS) ₂	3280 mbr	1510 br	710 ms	625 vw	2080 ms	800 s
u (NCS) ₂	3364 s	1496 sh	705 s	632 s	...	...
(NCS) ₂	3370 mbr	1518 ms	698 s	630 vw	2070 s	800 msh
(NCS) ₂	3238 mbr	1495 mbr	680 mbr	612 vw	2060 s	815 ms
(NCS) ₂	3328 s	1483 ms	754 s	631 s	...	...
(NCS) ₂	3380 ms	1503 ms	748 s	610 br	2010 s	790 wsh
(NCS) ₃	3290 mbr	1510 mbr	745 ms	...	2050 w	810 ms
l (NCS) ₂	3374 s	1508 ms	779 s	632 ms	...	...
(NCS) ₂	3350 br	1510 br	770 s	610 wbr	2115 s	800 wsh
(NCS) ₂	3200 wbr	1520 mbr	769 s	610 vw	2070 s	820 s
(NCS) ₂	3372 vs	1514 ms	745 s	643 ms	...	...
(NCS) ₂	3390 ms	1500-10 br	748 ms	640 vw	2050 vs	810 w
(NCS) ₂	3400 ms	1510 mbr	752 wbr	625 vw	2060 s	800 s
Ptu (NCS) ₂	3414 s	1489 ms	773 s	692 vs	...	...
(NCS) ₂	3390 mbr	1474 ms	760 s	680 mbr	2062 vs	770 wsh
(NCS) ₂	3400 ms	1498 ms	772 ms	690 vw	2050 s	810 s
Ptu (NCS) ₂	3378 s	1500 s	753 ms	660 ms	...	...
(NCS) ₂	3350 vs	1490 br	753 ms	670 ms	2060 ms	...
(NCS) ₂	3270 w	1500 mbr	...	672 ms	2065 s	810 s
tu (NCS) ₂	3354 wsh	1510 ms	...	640 w	...	...
(NCS) ₂	3365 wbr	1515 ms	...	640 vw	2060 vs	...
(NCS) ₂	3280 wsh	1500 mbr	...	640 mbr	2055 s	810 mw

s = sharp ; br = broad ; vs = very sharp ; ms = medium sharp ; mbr = medium broad ; sh = shoulder.

Sl. No.	ν_1 kK	ν_2 kK	ν_3 kK	β'	β'	ν_2/ν_1	Δcm^{-1}	μ_{eff} BM
1.	8.477	14.930	22.779	892.6	0.845	1.76	8477	2.94
2.	8.696	15.620	26.666	1010.7	0.957	1.79	8696	2.89
3.	8.513	14.930	22.222	852.3	0.807	1.75	8513	3.01
4.	Diamagnetic							
5.	9.804	16.530	24.390	1007.6	0.954	1.69	9804	2.87
6.	8.510	14.930	25.000	1050.6	0.995	1.75	8510	2.94
7.	8.333	14.710	25.641	973.2	0.922	1.76	8333	2.85
8.	9.291	16.130	25.979	982.0	0.930	1.73	9291	3.00
9.	8.333	14.070	24.691	900.3	0.855	1.76	8333	2.80
10.		7.074	16.670	764.8	0.780	...	4092	4.64
11.		7.113	11.670	672.8	0.690	...	4114	4.72
12.		5.780	15.500	756.0	0.770	...	3314	4.54
13.		7.885	16.320	692.9	0.709	...	4590	4.50
14.		6.945	16.130	734.4	0.750	...	4020	4.64
15.		7.756	16.130	684.1	0.700	...	4541	4.41
16.		7.264	16.260	724.7	0.724	...	4217	4.81
17.		7.268	16.000	705.8	0.723	...	4227	4.62
18.		7.724	16.260	696.2	0.713	...	4514	4.48

cobalt (II) or nickel (II) ion (Nakamoto 1970 ; Mitchell and Williams 1960 ; Sabatini and Bertini 1965). However an extra band at 2140 cm^{-1} exhibited by *m*-Cl Ptu and *m*-NO₂ ptu may tempt us to assign that for S bonding of NCS group, the position of ν_{CS} band does not support the above view. If the thiocyanate complexes were to be S bonded, the ν_{CN} should appear at a higher frequency side and ν_{CS} at lower frequency ($690\text{--}720 \text{ cm}^{-1}$). Thus it can be concluded that in our complexes thiourea and thiocyanate are bonded through S and N respectively.

3.3. Electronic spectra

The solid state electronic spectra of the present nickel complexes exhibit three bands at $\sim 8,500 [{}^3T_{2g} \leftarrow {}^3A_{2g}(F) \nu_1]$, $\sim 15,000 [{}^3T_{1g}(F) \leftarrow {}^3A_{2g}(F) \nu_2]$ and $\sim 24,000 [{}^3T_{1g}(P) \leftarrow {}^3A_{2g}(F) \nu_3]$. The spectral parameters such as Δ ($10\Delta_{\text{Dq}}$) and β have been calculated (Drago 1965). The octahedral nature of the complexes has been proved by the very weak intensity of the bands and the low value of ν_2/ν_1 (1.73 to 1.79) [Sutton 1968]. The extent of covalency of the metal ligand bond can be estimated from β as shown in table 3.

In a tetrahedral ligand field, the frequencies of transition for cobalt (II) ion ${}^4T_2(F) \leftarrow {}^4A_2(F)$, ${}^4T_1(P) \leftarrow {}^4A_2(F)$ and ${}^4T_1(F) \leftarrow {}^4A_2(F)$ are designated as ν_1 (not found) ν_2 ($\sim 16,000 \text{ cm}^{-1}$) and ν_3 ($\sim 7000 \text{ cm}^{-1}$) respectively in the increasing order of energies. The ligand field and Racah parameters have been calculated (Cotton and Goodgame 1961) and presented in table 3.

the rule of average environment CoS_2Cl_2 chromophore-Dq ($302\text{--}401\text{ cm}^{-1}$), B' ($625\text{--}697\text{ cm}^{-1}$) and suggest that in these chloro-complexes, the ligand molecules are coordinated through S atom of the CS group.

3.4. Magnetic susceptibility data

It is observed that the μ_{eff} values of Ni(II) complexes lie in the range 2.8 to 3.00 BM. As these values are slightly above the spin only value (2.83 BM), it is evident that the present complexes (1 to 9 excluding 4) are octahedral in nature and the complex 4 is square planar. The magnetic susceptibility values of Co(II) complexes lie in the range 4.4–4.8 BM which are higher than spin only value (3.87 BM). This indicates tetrahedral nature of the complexes.

4. Conclusion

On the basis of the above analytical, spectral and magnetic data, the tentative structure proposed for $\text{NiL}_2(\text{SCN})_2$ is shown below.

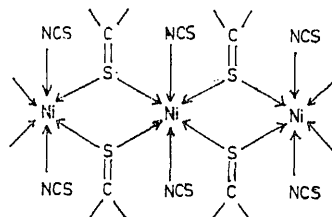


Figure 1. Structure of $[\text{Ni}(\text{o-Cl Ptu})_2(\text{SCN})(\text{NCS})]$ complex.

Thus the octahedral nature of the central metal is indicated. However it is to be recognized that cobalt complexes exist as monomers with tetrahedral symmetry.

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Optical absorption spectrum of thulium nitrate in solution

S V J LAKSHMAN* and C K JAYASANKAR

Spectroscopic Laboratories, Department of Physics, S V University, Tirupati 517 502, India

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Abstract. Spectral investigation of Tm^{3+} in thulium nitrate has been carried out. For the first time, the second derivative spectrum of this complex has been recorded. The results of a least squares fit of the energy levels and oscillator strengths of the bands are reported in terms of interaction parameters and Judd-Ofelt parameters. Radiative transition probabilities for fluorescence levels 3P_0 , 1I_6 , 1D_2 and 1G_4 of Tm^{3+} in thulium nitrate are estimated.

Keywords. Thulium nitrate; optical absorption; derivative spectrum; transition probabilities.

1. Introduction

Considerable progress has been made in interpreting the optical spectra of Tm^{3+} ion embedded in crystalline solids (Dieke 1968), in different solution media (Carnall *et al* 1965, 1968) and in glasses (Reisfeld 1975).

Since no detailed investigation of the optical absorption spectrum of thulium nitrate has so far been reported in literature, the authors took up the present investigation of work. For the first time, derivative spectrum of this sample has been studied by the authors.

2. Experimental

Thulium Nitrate solution of 0.1 mole percent was prepared. Normal and second derivative spectrum in the wavelength region 8300 Å–2300 Å were recorded on a Perkin-Elmer 551 recording spectrophotometer.

The near infrared spectrum in the wavelength region of 11100 Å–14300 Å was recorded on a Carl-Zeiss Specord 61 recording spectrophotometer. Second derivative spectrum could not be recorded in this region as there is no derivative accessory for this NIR instrument. The refractive index of the solution was measured on a PZO WARSZANARL Nr 3275 refractometer.

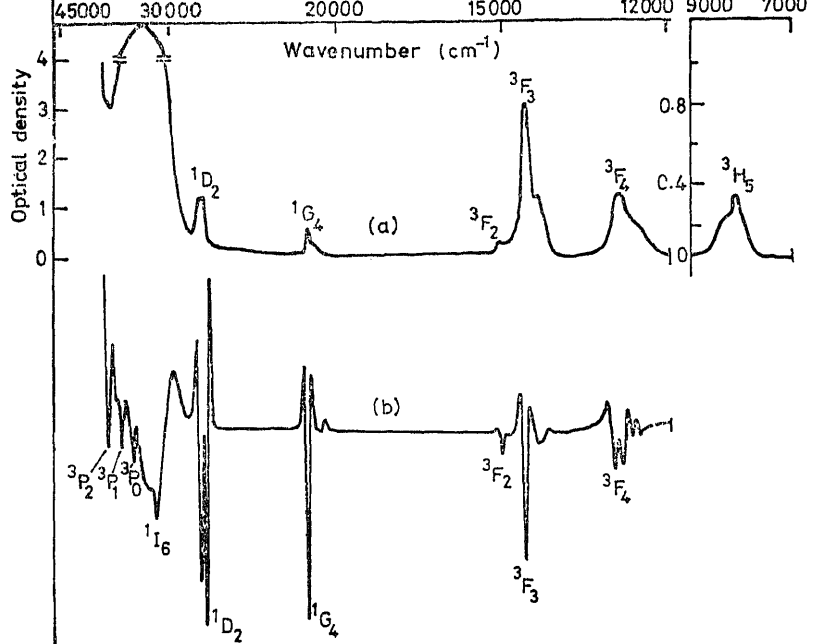


Figure 1. Absorption spectrum of thulium nitrate solution. (a) normal spectrum (b) second derivative spectrum.

3. Results and analysis

3.1. Energy levels

Under the influence of an electric field of the solution matrix, the changes in the parameters E^k ($k = 1, 2, 3$) and ξ_{4f} are very small. To a first order approximation therefore, the energy E_J of the J th level may be expressed by a Taylor-series expansion as follows

$$E_J = E_{0J} + \frac{dE_J}{dE^1} \Delta E^1 + \frac{dE_J}{dE^2} \Delta E^2 + \frac{dE_J}{dE^3} \Delta E^3 + \frac{dE_J}{d\xi_{4f}} \Delta \xi_{4f} + \frac{dE_J}{da} \Delta a + \frac{dE_J}{d\beta} \Delta \beta \quad (1)$$

where E_{0J} is the zero-order energy of the level J , and dE_J/dE^k , $dE_J/d\xi_{4f}$, dE_J/da and $dE_J/d\beta$ are the partial derivatives. Further

$$\Delta E^k = E^k - E^{k0}$$

$$\Delta \xi_{4f} = \xi_{4f} - \xi_{4f}^0$$

$$\Delta a = a - a^0$$

Table 1. Experimental and calculated energy levels and spectroscopic parameters for $\text{Tm}^{3+} : \text{Tm}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$.

Energy level	E_{exp} (cm^{-1})	E_{cal} (cm^{-1})	Parameters (cm^{-1})
$^3\text{H}_4$	...	5736	$E^1 = 6533 \cdot 02$
$^3\text{H}_5$	8090	8377	$E^2 = 31 \cdot 222$
$^3\text{F}_4$	12833	12788	$E^3 = 642 \cdot 493$
$^3\text{F}_3$	14648	14675	$\xi_{4f} = 2680 \cdot 54$
$^3\text{F}_2$	15193	15089	$a = -39 \cdot 889$
$^1\text{G}_4$	21546	21531	$\beta = 405 \cdot 382$
$^1\text{D}_2$	27770	27930	
$^1\text{I}_6$	32511	32492	
$^3\text{P}_0$	35263	35483	
$^3\text{P}_1$	36686	36478	
$^3\text{P}_2$	38376	38246	
$^1\text{S}_0$	...	74743	
RMS deviation.	$\pm 152 \text{ cm}^{-1}$		

where E^{k0} , ${}^9_4\xi_f$, a_0 and β^0 are the free ion parameters and E^k , ξ_{4f} , a and β are the parameters of the ion in the crystal or solution matrix.

Figure 1 shows the normal and second derivative spectra of thulium nitrate. The assignments of electronic transitions to the observed bands was straight forward.

For the numerical evaluation of the E^k , ξ_{4f} , a and β parameters, the observed energy levels were substituted for E_J in (1). The values of the zero-order energies and partial derivatives were taken from the data given by Lakshman and Jayasankar (1982). With the linear equations thus formed which are equal to the number of observed levels, the values of ΔE^k , $\Delta \xi_{4f}$, Δa and $\Delta \beta$ were evaluated by the least square fit method. From these delta values, the parameters E^k , ξ_{4f} , a and β for Tm^{3+} in thulium nitrate were calculated using the formula given in (2) and are presented in table 1. The energy levels calculated using the above parameters are presented in table 1 along with the observed band positions. The wavefunctions in the intermediate scheme are given in table 2.

3.2. Spectral intensities and transition probabilities

The oscillator strengths and the Judd-Ofelt parameters (T_λ and Ω_λ) are evaluated

Table 2. Computed eigenvalues and eigenvectors for Tm^{3+} : $\text{Tm}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$.

Assignment from $^3\text{H}_6$	J	Eigenvalue	Eigenvector components
^3H	6	0	$0\cdot10156\ ^1\text{I} + 0\cdot99483\ ^3\text{H}$
^3H	4	5736	$-0\cdot28695\ ^3\text{H} + 0\cdot54776\ ^1\text{G} + 0\cdot78589\ ^3\text{F}$
^3H	5	8377	$1\cdot00000\ ^3\text{H}$
^3F	4	12788	$-0\cdot76768\ ^3\text{H} + 0\cdot35923\ ^1\text{G} - 0\cdot53068\ ^3\text{F}$
^3F	3	14675	$1\cdot00000\ ^3\text{F}$
^3F	2	15089	$-0\cdot86726\ ^3\text{F} + 0\cdot47633\ ^1\text{D} + 0\cdot14478\ ^3\text{P}$
^1G	4	21531	$0\cdot57301\ ^3\text{H} + 0\cdot75558\ ^1\text{G} - 0\cdot31742\ ^3\text{F}$
^1D	2	27930	$0\cdot45475\ ^3\text{F} + 0\cdot63958\ ^1\text{D} + 0\cdot61979\ ^3\text{P}$
^1I	6	32492	$-0\cdot99483\ ^1\text{I} + 0\cdot10156\ ^3\text{H}$
^3P	0	35483	$-0\cdot96980\ ^3\text{P} + 0\cdot24389\ ^1\text{S}$
^3P	1	36478	$1\cdot00000\ ^3\text{P}$
^3P	2	38246	$0\cdot20263\ ^3\text{F} + 0\cdot60336\ ^1\text{D} - 0\cdot77130\ ^3\text{P}$
^1S	0	74743	$0\cdot24389\ ^3\text{P} + 0\cdot96980\ ^1\text{S}$

Table 3. Experimental and calculated oscillator strengths and squared reduced matrix elements $(f^{12}\ ^3\text{H}_6 \parallel \text{U}^\lambda \parallel I^{12}\ S'L'J')^2$ for Tm^{3+} : $\text{Tm}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$.

$S'L'J'$	$f_{\text{exp}} \times 10^6$	$f_{\text{cal}} \times 10^6$	$(U^2)^2$	$(U^4)^2$	$(U^6)^2$
$^3\text{H}_5$	0.205	0.835	0.10722	0.23104	0.63730
$^3\text{F}_4$	1.746	1.274	0.24158	0.11109	0.60523
$^3\text{F}_3$	2.071	1.625	0	0.31588	0.83973
$^3\text{F}_2$	0.184	0.162	0	0.00002	0.25724
$^1\text{G}_4$	0.343	0.584	0.04735	0.07140	0.01389
$^1\text{D}_2$	2.634	2.180	0	0.30913	0.09402

RMS deviation 0.425×10^{-6}

Refractive Index (n) = 1.3363

 $T_1 = 0.10647 \times 10^{-9}$; $T_2 = 0.24137 \times 10^{-9}$; $T_3 = 0.04132 \times 10^{-9}$; $Q_1 = 1.07544 \times 10^{-20}$; $Q_2 = 0.00000 \times 10^{-20}$; $Q_3 = 0.00000 \times 10^{-20}$

SLJ (1)	SLJ'	(U ²) ² (3)	(U ¹) ² (4)	(U ⁰) ² (5)	S _{ed} /e ² × 10 ²² (6)	S _{md} /e ² × 10 ²² (7)	f × 10 ⁶ (8)	A (9)
³ P ₀	¹ I ₆	0	0	0.02468	1.025	0	0.036	0
	¹ D ₂	0.02574	0	0	5.085	0	0.492	33
	¹ G ₄	0	0.04441	0	10.778	0	1.911	424
	³ F ₂	0.36286	0	0	71.681	0	18.592	3829
	³ F ₃	0	0	0	0	0	0	0
	³ F ₄	0	0.02184	0	5.300	0	1.536	911
	³ H ₆	0	0	0	0	0	0	0
	³ H ₄	0	0.28125	0	68.257	0	26.046	26771
	³ H ₅	0	0	0.07649	3.178	0	1.448	2123
						A _T = 39091, τ _R = 25.6 μ sec		
¹ I ₆	¹ D ₂	0	0.04915	0.83918	46.793	0	0.221	6
	¹ G ₄	0.21489	1.25563	0.62913	373.317	0	4.069	577
	³ F ₂	0	0.04282	0.36864	25.708	0	0.443	156
	³ F ₃	0	0.00329	0.00875	1.162	0	0.021	8
	³ F ₄	0.06760	0.30670	0.09205	91.611	0	1.792	818
	³ H ₆	0.00112	0.00241	0.00664	1.082	0	0.026	18
	³ H ₄	0.06022	0.49757	0.39987	149.264	0	3.973	3358
	³ H ₅	0.01257	0.04604	0.01590	14.317	0.57710	0.484	603
						A _T = 5540, τ _R = 180.4 μ sec.		
	¹ G ₄	0.19388	0.17705	0.00102	81.310	0	1.308	60
	³ F ₂	0.06436	0.30263	0	86.159	3.47676	2.928	546
	³ F ₃	0.16117	0.06476	0	47.555	0	1.613	327
	³ F ₄	0.13396	0.01331	0.23164	39.317	0	1.518	399
	³ H ₅	0	0.00049	0.02316	1.081	0	0.055	25
	³ H ₄	0.54629	0.09609	0.02223	132.160	0	7.527	4308
	³ H ₆	0	0.30913	0.09402	78.929	0	5.665	5151
¹ G ₄						A _T = 10816, τ _R = 92.5 μ sec.		
	³ F ₂	0.00455	0.06836	0.04173	19.223	0	0.175	8
	³ F ₃	0.01029	0.07242	0.30450	32.259	0	0.320	18
	³ F ₄	0.15855	0.00386	0.37120	47.679	11.35248	0.756	68
	³ H ₅	0.07376	0.00554	0.54331	38.488	0	0.744	156
	³ H ₄	0.00329	0.01981	0.07436	8.547	0.58331	0.209	62
	³ H ₆	0.04735	0.07140	0.01389	27.259	0	0.843	462
						A _T = 777, τ _R = 1287.0 μ sec.		

The total radiative transition probability for a transition $\psi J \rightarrow \psi' J'$ is given by

$$A(\psi J : \psi' J') = \frac{64\pi^4 \sigma^3}{3h(2J+1)} \left(\frac{n(n^2+2)^2}{9} S_{ed} + n^3 S_{md} \right) \quad (3)$$

where the symbols have their usual significance (Reisfeld 1975). Since the excited state relaxation usually involves transition to a number of states, we define a total radiative relaxation rate

$$A_T(\psi J) = \sum_{\psi' J'} A(\psi J : \psi' J') \quad (4)$$

where the sum runs over all $\psi' J'$ lower in energy than ψJ . The radiative lifetime of a state is

$$\tau_R(\psi J) = (A_T(\psi J))^{-1} \quad (5)$$

The calculated radiative lifetimes are given in table 4.

4. Discussion

The radiative lifetime for Tm^{3+} in thulium nitrate is highest in 1G_4 , while it is least in 3P_0 level. Similar results have been reported in glasses also (Reisfeld 1975). Second derivative spectra exhibit (figure 1b) splittings in 3F_4 , 3F_3 , 1G_4 and 1D_2 levels. Since the crystal symmetry for Tm^{3+} in thulium nitrate is not clearly known, no attempt to calculate the approximate crystal field parameters could be made. It is interesting to note that the closely lying 1I_6 , 3P_0 , 3P_1 and 3P_2 levels are very well resolved in the second derivative spectrum as is seen in figure 1b.

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Studies on the electrochemical and thermodynamic behaviour of tin-tin sulphide electrode in the presence of sulphide ions

PUSHPA SHARMA and MUKHTAR SINGH*

Department of Chemistry, Agra College, Agra 282 002, India

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Abstract. Tin-tin sulphide (Sn-SnS) electrode has been prepared. Statistical analysis indicates that this electrode is stable and reproducible. It has been found that the electrode can be used in the quantitative determination of S^{2-} in the presence of foreign ions such as F^- , Cl^- , Br^- , I^- , HCO_3^- , CO_3^{2-} , SO_3^{2-} , SO_4^{2-} and NO_3^- . The potential of the electrode in the presence of S^{2-} has been measured by setting up the following type of cell: Sn-SnS/ S^{2-} (saturated) KCl/ Hg_2Cl_2 , Hg. The electrode shows Nernstian response to pS ($-\log[S^{2-}]$) over the range 7.09 to 12.26. The electrode also shows the Nernstian response to pH in the range 7.54 to 11.98 at constant pS. Values of E^0 , $(\partial E^0/\partial T)_P$ and various thermodynamic functions, viz., ΔG^0 , ΔH^0 and ΔS^0 for the electrode reaction, $Sn_{(s)} + S^{2-}_{(aq)} \rightleftharpoons SnS_{(s)} + 2e$, have been determined. Besides, the standard free energy of formation (ΔG_f^0) and solubility product constant (K_{sp}) of SnS in aqueous medium at $25 \pm 0.1^\circ C$ have also been determined.

Keywords. Tin-tin sulphide electrode; sulphide ions; thermodynamic behaviour.

1. Introduction

In continuation to earlier publications (Sharma and Singh (in press)) we now report our results of investigation on the electrochemical and thermodynamic behaviour of Sn-SnS electrode in the presence of sulphide ions under different experimental conditions.

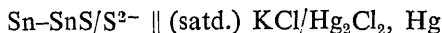
2. Experimental

The tin-tin sulphide (Sn-SnS) electrode was prepared by the same general method as reported in earlier publications (Sharma and Singh). All the chemicals used were of analytical reagent grade. Stock solutions were prepared in double distilled water. A series of Britton Robinson (BR) buffers of pH 7.54 to 11.98

* To whom all correspondence should be made.

addition of normal solution of sodium hydroxide. Stock solutions of sodium sulphide were prepared by dissolving reagent grade $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ in double distilled water, and standardised by Bethge (1954) method. A series of stock solutions of Na_2S were prepared keeping the ionic strength constant at 0.02 M by addition of an appropriate volume of NaNO_3 . pH readings were converted to hydrogen ion concentration.

The potential of the electrode in solutions containing S^{2-} was measured at $25 \pm 0.1^\circ \text{C}$ by setting up the following type of cell :



3. Results and discussion

Sn-SnS electrode was prepared six times under identical conditions and each time its potential was measured in well-stirred aqueous Na_2S solutions of different concentrations (6.0×10^{-6} , 4.0×10^{-5} , 6.0×10^{-4} and $2.9 \times 10^{-3} \text{ M}$) at $25 \pm 0.1^\circ \text{C}$. The results indicated that the variation in the value of electrode potential was within the limits of standard deviation (1.8×10^{-3}) which shows that the potential of the electrode is reproducible.

The potential of Sn-SnS electrode was measured in aqueous Na_2S solutions of different concentrations (6.0×10^{-6} , 4.0×10^{-5} , 6.0×10^{-4} and $2.9 \times 10^{-3} \text{ M}$) at $25 \pm 0.1^\circ \text{C}$. It was found that the potential of the electrode became constant within one minute of its immersion in well-stirred solutions. It is thus inferred that the electrode attains equilibrium potential rapidly.

The potential of Sn-SnS electrode was measured in aqueous solutions of Na_2S of different concentrations (6.0×10^{-6} , 4.0×10^{-5} , 6.0×10^{-4} and $2.9 \times 10^{-3} \text{ M}$) after an interval of one month at $25 \pm 0.1^\circ \text{C}$. It was found that the potential of the electrode remained steady up to 10 months. This study reveals that the electrode is fairly stable if handled carefully and kept in double distilled water after use. However, if the electrode was allowed to remain in the atmosphere for a few hours it began to give erratic readings.

3.1. *Electrochemical behaviour of Sn-SnS electrode vis-a-vis its use in the quantitative determination of sulphide ion concentration.*

A series of aqueous solutions of Na_2S of different concentrations ranging from 6.0×10^{-6} to $4.0 \times 10^{-3} \text{ M}$ were prepared keeping the ionic strength constant at 0.02 M . The potential of the electrode (v. SCE) was measured as a function of $[\text{S}^{2-}]$ at $25 \pm 0.1^\circ \text{C}$. The pH of the solutions was measured with the help of Philips pH-meter (PR 9405) and $[\text{S}^{2-}]$ was calculated at different $[\text{S}^{2-}]$, according to the procedure reported in earlier publication (Sharma and Singh (in press)). The plot of $E_{\text{Sn-SnS}}$ vs $\log [\text{S}^{2-}]$ is linear (figure 1). The electrochemical equation to this linear plot (figure 1) has been obtained as under :

$$E_{\text{Sn-SnS}} = -0.610 - 0.030 \log [\text{S}^{2-}] \quad (1)$$

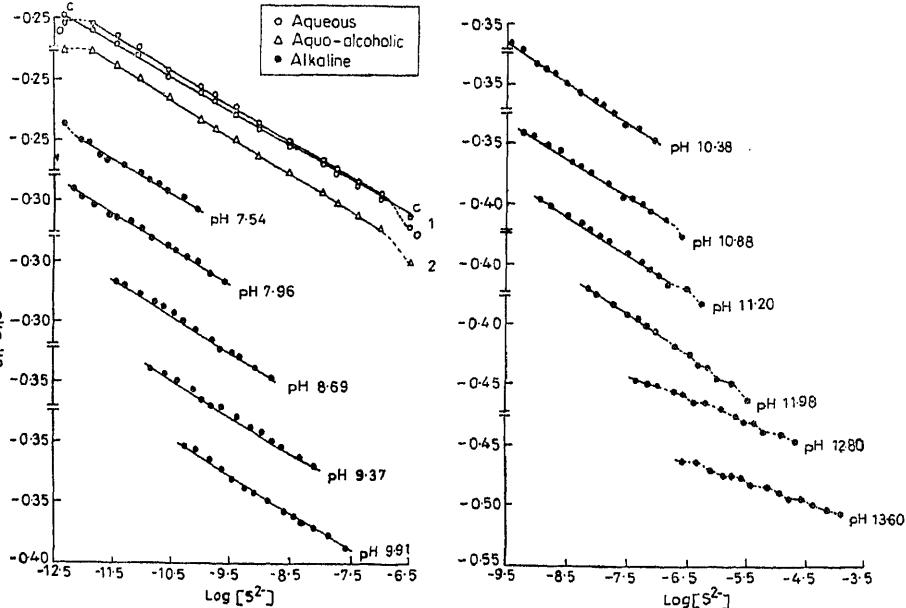


Figure 1. Plots of $E_{\text{Sn-SnS}}$ (volts) vs SCE against $\log [S^{2-}]$ in aqueous, aquo-alcoholic (50% v/v) and alkaline (pH 7.54–13.60) media at $25 \pm 0.1^\circ \text{C}$. (O = observed) (C = calculated).

where the intercept potential value -0.610 V at $\log [S^{2-}] = 0$ is the algebraic sum of the standard electrode potential (E^0) of Sn-SnS electrode and that of SCE from which E^0 of the electrode works out to be -0.851 V at $25 \pm 0.1^\circ \text{C}$.

The validity of the above electrochemical equation (1) has been further checked by obtaining the calculated values of potential of Sn-SnS electrode as a function of $\log [S^{2-}]$ by applying the regression analysis (Brown and Saltee 1963). From Figure 1 it is evident that the calculated and observed values are almost the same. The variance of electrode potential about $\log [S^{2-}]$ is 7.3×10^{-6} and the standard deviation is 0.27% . Since these values are very small in comparison with the calculated values of electrode potential it is concluded that the assumed relation is justified. Thus Sn-SnS electrode can be successfully used in the quantitative determination of S^{2-} in given samples.

2. Influence of various experimental conditions on the working of tin-tin sulphide electrode

2a. *Influence of foreign ions* : The effect of the presence of some foreign ions such as F^- , Cl^- , Br^- , I^- , HCO_3^- , CO_3^{2-} , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, SO_4^{2-} , NO_2^- and NO_3^- with their increasing concentrations (1×10^{-6} – $1 \times 10^{-1} \text{ M}$) was investigated on the working of Sn-SnS electrode in $1 \times 10^{-4} \text{ M}$ sodium sulphide solution. The results of the study indicates that there is hardly any difference between the

I⁻, HCO₃⁻, CO₃²⁻, SO₃²⁻, SO₄²⁻ and NO₃⁻ ions. From this study it follows that Sn-SnS electrode can be successfully used in the quantitative determination of sulphide ions in presence of impurities of F⁻, Cl⁻, Br⁻, I⁻, HCO₃⁻, CO₃²⁻, SO₃²⁻, SO₄²⁻ and NO₃⁻ ions in the given samples.

3.2b. *Effect of medium* : The working of the electrode was studied in alcoholic solution of Na₂S of varying concentrations ranging from 6.0×10^{-6} to 2.9×10^{-3} M. The potential of Sn-SnS electrode was measured as a function of [S²⁻] in 50% (v/v) alcoholic solutions of Na₂S at $25 \pm 0.1^\circ$ C. The plots of $E_{\text{Sn-SnS}}$ vs $\log [S^{2-}]$ are linear (figure 1). This shows that the electrode can be successfully used in the quantitative determination of sulphide ion in aquo-alcoholic medium. The electrochemical equation to the linear plot (figure 1) of Sn-SnS electrode can be represented as under :

$$E_{\text{Sn-SnS}} = -0.640 - 0.031 \log [S^{2-}] \text{ for } 50\% \text{ (v/v)} \quad (2)$$

The value of E^0 works out to be -0.881 V and the experimental slope value is 0.031 V. The validity of above electrochemical equation is justified by the statistical treatment of data which shows a variance of 8.4×10^{-6} and standard error 0.29% . The electrode was also tried in non-aqueous (100% alcohol) medium but it failed to respond to S²⁻.

3.2c. *Effect of pH (BR buffer)* : A series of Na₂S solutions of varying concentrations ranging from 6.0×10^{-6} to 2.9×10^{-3} M were prepared in BR buffer (pH 7.54-11.98) and in solution of pH 12.80 and 13.60 ; and [S²⁻] was calculated (Sharma and Singh (in press)) at different pH values. The potential of the electrode has been measured as a function of [S²⁻] at fixed (controlled) pH values (7.54-13.60). The plots of $E_{\text{Sn-SnS}}$ vs $\log [S^{2-}]$ were found to be linear (figure 1). These indicate a Nernstian response with slope of 0.030 V in the pS range 7.09 - 12.26 at $25 \pm 0.1^\circ$ C and is within the experimental error of the theoretical value given by equation :

$$E_{\text{Sn-SnS}} = \text{constant} - 0.0296 \log [S^{2-}] \quad (3)$$

where the 'constant' is the sum of standard electrode potentials of the saturated calomel electrode and the standard potential of Sn-SnS electrode. Also the potential of Sn-SnS electrode was measured as a function of pH values (≥ 7.54) keeping the sulphide ion concentration constant. At constant [S²⁻], and constant ionic strength 0.02 M (NaNO₃) a plot of $E_{\text{Sn-SnS}}$ vs pH is linear (figure 2) having an experimental slope of 0.030 ± 0.004 V per pH unit. The Sn-SnS electrode can thus be used to measure pH between 7.54-11.98 at given [S²⁻]. A perusal of this study reveals that Sn-SnS electrode can be successfully used in the quantitative determination of sulphide ion in alkaline medium from pS ($-\log [S^{2-}]$) 7.09 to 12.26 and in the pH range 7.54 - 11.98.

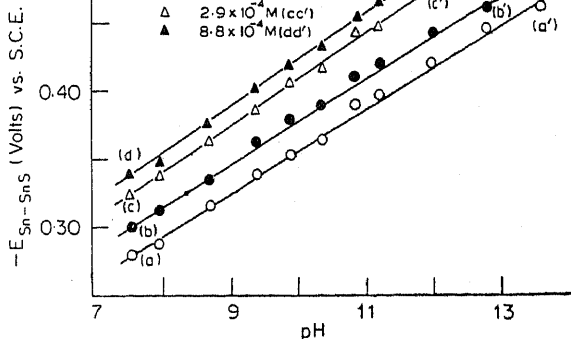


Figure 2. Plots of $E_{\text{Sn-SnS}}$ (volts) vs SCE against pH at constant sodium sulphide concentration ($[S^{2-}]_0$).

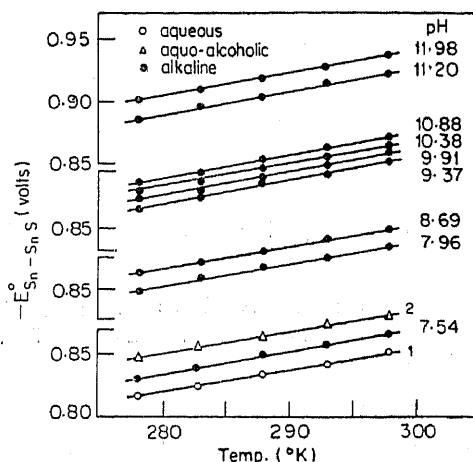


Figure 3. Plots of $E_{\text{Sn-SnS}}^0$ (volts) vs temperature ($^{\circ}\text{K}$) in aqueous, aquo-alcoholic (50 % v/v) and alkaline (pH 7.54–11.98) media containing S^{2-} .

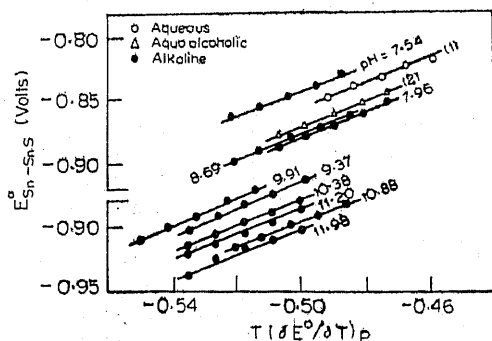


Figure 4. Plots of $E_{\text{Sn-SnS}}^0$ (volts) vs $T(\Delta E^0/\Delta T)_p$ in aqueous, aquo-alcoholic (50% v/v) and alkaline (pH 7.54–11.98) media containing S^{2-} .

different concentrations of Na_2S in aqueous, aquo-alcoholic (50% v/v) and alkaline (pH 7.54–11.98) solutions. From the plots of $E_{\text{Sn-SnS}}$ vs $\log [\text{S}^{2-}]$ at different temperatures in various media, the values of E^0 of electrode have been obtained at different temperatures. The temperature coefficient, $(\partial E^0/\partial T)$, of E^0 has also been determined from the linear plots of E^0 (volts) vs T ($^{\circ}\text{K}$) (figure 3), in various media. The corresponding values of $T(\partial E^0/\partial T)_P$ have been calculated and the relationship between $T(\partial E^0/\partial T)_P$ and E^0 in different media containing S^{2-} has been shown in figure 4. The relationship is linear in all the cases in accordance with the equation:

$$E^0 = -\frac{\Delta H^0}{nF} + T\left(\frac{\partial E^0}{\partial T}\right)_P \quad (4)$$

The thermodynamic functions (Daniels and Alberty 1966) ΔH^0 , ΔG^0 and ΔS^0 for Sn-SnS electrode in different media at $25 \pm 0.1^{\circ}\text{C}$ containing S^{2-} , have been calculated and the values listed in table 1.

3.3. The standard free energy of formation (ΔG_f^0) of SnS

The standard free energy of formation, ΔG_f^0 , of SnS can be calculated following the method put forward by Goates *et al* (1951) for the calculation of ΔG_f^0 of Ag_2S . Now, ΔG^0 for Sn-SnS electrode, *i.e.*, for the electrode reaction,

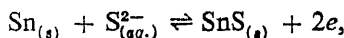


Table 1. Values of various thermodynamic parameters for Sn-SnS electrode in aqueous, aquo-alcoholic (50% v/v) and alkaline (pH 7.54–11.98) solutions of S^{2-} at $25 \pm 0.1^{\circ}\text{C}$.

Medium	ΔG^0 kcal mole $^{-1}$	ΔH^0 kcal mole $^{-1}$	ΔS^0 e.u.
Aqueous	39.3	16.6	-76.1
Aquo-alcoholic (50% v/v)	40.7	17.3	-78.4
Alkaline (pH)			
7.54	39.9	15.8	-80.8
7.96	40.8	17.4	-78.4
8.69	41.5	17.4	-80.8
9.37	41.6	16.8	-83.1
9.91	42.0	16.6	-85.4
10.38	42.3	17.5	-83.1
10.80	42.4	18.3	-80.8
11.20	42.5	17.7	-83.1
11.98	43.2	18.4	-83.1

shows that the above electrode reaction is nonspontaneous in the forward direction and that in the backward direction it would be spontaneous with $\Delta G^0 = -39.3$ kcal. Thus,

$$-39.3 = \Delta G_f^0 (\text{SnS}_{(s)}) - [\Delta G_f^0 (\text{Sn}_{(s)}) + \Delta G_f^0 (\text{S}_{(\text{aq})}^{2-})].$$

As ΔG_f^0 of $\text{Sn}_{(s)}$ (element) is zero and taking (Kaye and Laby 1959) ΔG_f^0 for S^{2-} as 20.00 kcal mole $^{-1}$ (at 25°C) the value of ΔG_f^0 of SnS works out to be -19.3 kcal mole $^{-1}$. This is in agreement, within the experimental accuracy, with the literature value (Lurie 1975) of -19.7 kcal mole $^{-1}$.

3.4. Solubility product constant (K_{sp}) of SnS

The solubility product constant, K_{sp} , of SnS can be calculated from the standard free energy change of the reaction :

$\text{SnS} \rightleftharpoons \text{Sn}^{2+} + \text{S}^{2-}$, by means of the expression (Goates *et al* 1951)

$$\ln K_{sp} = \frac{-\Delta G^0}{RT}$$

Since the values of ΔG_f^0 of SnS has already been calculated as -19.3 kcal mol $^{-1}$ and using the literature values (Kaye and Laby 1959) of ΔG_f^0 for S^{2-} and Sn^{2+} as 20.0 kcal and 6.28 kcal respectively, the value of K_{sp} can be obtained from the above equation. This works out to be 6.1×10^{-25} at $25 \pm 0.1^\circ\text{C}$. This compares fairly well with the literature value (Lurie 1975) 1.0×10^{-25} (at 25°C).

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Compliant fields for molecular interactions I : Lithium cation with carbonyl donors

A S N MURTHY * and SHOBA RANGANATHAN

Department of Chemistry, Indian Institute of Technology, New Delhi 110 016, India

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Abstract. The CNDO/Force method has been employed in the determination of quadratic potential functions for the complexes of lithium cation with formaldehyde and formamide. The O, Li⁺ stretching frequency and the COLi⁺ bending frequencies have been estimated after scaling, the stretching and stretch-stretch elements of the force constant matrix. The transferability of the donor potential function to the complex has been verified.

Keywords. Ion-molecular interactions ; CNDO/Force method ; compliance constants.

1. Introduction

Alkali metal salts dissolved in non-aqueous electron-donor solvents give rise to characteristic bands of low frequency in the infrared spectrum, which have been attributed to metal ion-solvent cage vibrations (Rao 1973 ; Kecki 1973 ; Gardiner 1977 ; Irish and Brooker 1976). In the case of lithium cation, for example, this band appears around 400 cm⁻¹ and is largely dependent on the polarity of the solvent as well as the nature of the anion. In order to gain some insight into the nature of ion-molecule interactions, a simple 1 : 1 model containing one solvent molecule associated with one ion finds considerable application. This two body potential is expected to dominate in much more complicated situations existing in the actual liquid state (Schuster *et al* 1975a). The 'supermolecule' approach (Pullman and Pullman 1975) in which an ion and its attendant solvent molecule (or molecules) are treated as a single molecular entity, facilitates the use of quantum chemical molecular orbital methods in investigating ion-molecule interactions theoretically. Rao (1976) has extensively reviewed the work done in the study of metal-ligand interactions.

Wong *et al* (1971) have studied the interaction of alkali metal ions with acetone and have reported ion-oxygen stretching vibrational frequencies : for the interaction of Li⁺ with acetone this frequency occurs around 425 cm⁻¹. The influence

* To whom all correspondence should be made.

of electrolytes on the fundamental frequencies of acetone have also been reported by several workers (Pullin and Pollock 1958; Yamada 1960; Gulik-Krzywicki and Kecki 1965; Perelygin 1969; Gadzhiev and Pominov 1965; Driessen and Groeneveld 1969). The C=O stretching frequency has either been split or shifted to lower frequencies in these studies. The influence of electrolytes on the vibrational spectrum of formamide has been the subject of several investigations (Perelygin *et al* 1968; Gardiner *et al* 1975; Bukowska 1978; Rao *et al* 1972; 1973, 1979; Lees *et al* 1979). In the study by Lees *et al* (1979), the Li⁺—O stretching vibration has been observed at about 370 cm⁻¹ for LiCl : 2.5 HCONH₂. Absorption in the range 355–370 cm⁻¹ has been reported by Lees and coworkers (1979) for lithium salts in general.

In contrast to several experimental reports on metal-solvent cage vibrations in the range 200–500 cm⁻¹, very few theoretical calculations to predict these vibrations have been attempted, even at the *ab initio* level. Most theoretical studies of ion-molecule interactions have been confined to the energetics of interaction and these studies have been reviewed by Schuster and coworkers (1975a). The Li⁺—O stretching force constant in lithium-formaldehyde complex, used as a model for studying the Li⁺—acetone system, has been calculated by Gupta and Rao (1973). The *ab initio* calculations of Sadlej (1980) on the Li⁺—H₂CO, system show that the C=O stretching force constant is larger than that in H₂CO which although in accordance with the CNDO/2 calculations of Sadlej and Kecki (1971) on the interaction of acetone with a cation, is contrary to what one would expect following interaction involving electron donation. In the case of the Li⁺—formamide complex, the metal-oxygen stretching force constant has been estimated by the CNDO/2 energy method by Gupta and Rao (1973). Recently, Bukowska and Miaskiewicz (1981) have investigated the vibrational frequency shifts of three characteristic stretching modes of formamide (CO, NH and CN) and have estimated the force constants for the complex formed, by CNDO/2 energy method. However, no attempt has been made to estimate or experimentally determine the Li⁺—O stretching frequency. In several of the studies cited above complete optimization of the geometry of the 'supermolecule' has not been effected and optimization of the O—Li⁺ distance alone has been carried out, the rest of the molecule being constrained to the experimental geometry.

In recent years, quantum chemical methods have been increasingly used to calculate potential functions of molecules (Pulay 1976; Duncan 1975). Pulay and Torok (1973, 1978) have applied the force method (Pulay 1969) to CNDO/2 wave functions and have calculated equilibrium geometries as well as quadratic force constants. Annamalai *et al* (1976, 1978, 1982) have also employed the CNDO/Force (CNDO/F) method to several molecules of interest. It has been observed in these studies that the stretching force constants (diagonal and off-diagonal) are overestimated by the CNDO/F method while other force constants are determined reasonably well. The MNDO-MOCIC method developed by Swanson *et al* (1978) is based on the compliance constant formalism advocated by Taylor and Pitzer (1947); Maslou (1949); Decius (1963) and Jones and Ryan (1970). Compliance constants being uniquely defined and independent of the definition of the basis coordinates, are expected to be transferable between chemi-

In view of the lack of meaningful data regarding ion-molecule interactions, it was considered interesting to optimize the geometries of 1:1 complexes of lithium cation with formaldehyde and formamide as well as to determine the force constants for these complexes by CNDO/F method. Redundancy-free internal compliance constants for the donor systems have already been calculated by Murthy and Ranganathan (1982d and e).

2. Theoretical approach

The force constants F_{ij} , defined as

$$F_{ij} = (\partial^2 E / \partial R_i \partial R_j)_0$$

where E is the total energy of the molecule and R_i, R_j are their internal coordinates, are evaluated by analytical differentiation of the energy followed by numerical differentiation of the forces obtained in the first step, with respect to the internal coordinates (Pulay 1969). Among the various semiempirical MO methods available, Torok and Pulay (1978) found the CNDO/2 and INDO methods to yield better results than MINDO/2. The CNDO/F calculations in the present study were carried out using a modified version (Kanakavel *et al* 1976) of the CNDO/2 computer program (Pople and Beveridge 1970), incorporating Pulay's procedure (1969). Starting with a trial geometry, the force acting on each atom is calculated and by allowing the atoms to relax in the direction of the forces, f_i , the equilibrium geometry is arrived at. The molecule at the equilibrium geometry is subjected to distortions describing the vibrations of the molecule, and the forces computed in each case. The deformations $\pm \Delta R_i$ in the i th internal coordinate are of the order of $\pm 0.01\text{\AA}$ for stretching modes and $\pm 1^\circ$ for bending modes. The internal forces are obtained by suitable transformation of the cartesian forces computed by the program (Kanakavel *et al* 1976). The force constants F_{ij} are evaluated from the internal forces f by numerical differentiation :

$$F_{ij} = - \Delta f_i / \Delta R_j ; \quad F_{ji} = - \Delta f_j / \Delta R_i \\ F_{ij} \approx F_{ji}.$$

The vibrational secular equation in terms of compliance constants is

$$[CK - \Phi E] = 0,$$

where C is the compliance constant matrix, K the kinetic energy matrix and Φ is a diagonal eigenvalue matrix of elements $\phi_i = (4\pi^2 c^2 v_i^2)^{-1}$. The compliance constant matrix is the inverse of the force constant matrix F and characterizes the molecule just as completely as the F matrix.

One of the important advantages of the use of compliants is that the C matrix is invariant to the choice of coordinates. Therefore, when redundancy conditions exist among the internal coordinates, the compliants involving the redundancy are uniquely defined as zero. This is not true of the force constants involving a redundancy, which become indeterminate. Also, as the compliants C_{ij} are dependent on the coordinates i or j alone and independent of other coordinates,

the method of Schachtschneider (1964) and the frequencies are calculated from the *C* and *G* matrices with the help of program COMPLY (Swanson and Ottinger). All the calculations were carried out on an ICL 2960 computer.

3. Results and discussion

The approximations involved in the semiempirical CNDO/2 method lead to unrealistic geometries for metal ion—electron donor complexes. Rao (1973)

Table 1. CNDO/F geometries* and interaction energies* of complexes of lithium cation with formaldehyde and formamide.

Bond parameter	Complex	Donor	Complex (Ref)†
Li⁺—H₂CO :			
<i>r</i> _{CO}	1.256	1.241	1.21°
<i>r</i> _{OLi⁺}	2.288	...	1.84
<i>r</i> _{CH}	1.113	1.114	1.12°
∠HCH	118.4	116.3	118.0°
∠COLi ⁺	180.0°	...	180.0
<i>E</i> _{INT}	31.2	...	44.2
Li⁺ — HCONH₂ :			
<i>r</i> _{CO}	1.284	1.263	1.212°
<i>r</i> _{OLi⁺}	2.248	...	1.71
<i>r</i> _{CH}	1.112	1.116	1.125
<i>r</i> _{CN}	1.343	1.358	1.368°
<i>r</i> _{NH(cis)}	1.064	1.060	1.027°
<i>r</i> _{NH(trans)}	1.062	1.057	1.027°
∠OCN	123.1	123.8	125.0°
∠HCN	117.4	115.3	112.7°
∠HNH	115.0	115.2	...
∠CNH (cis)	121.9	121.1	118.7°
∠CNH(trans)	123.1	123.7	119.7°
∠COLi ⁺	180.0°	...	180.0
<i>E</i> _{INT}	39.4	...	55.9

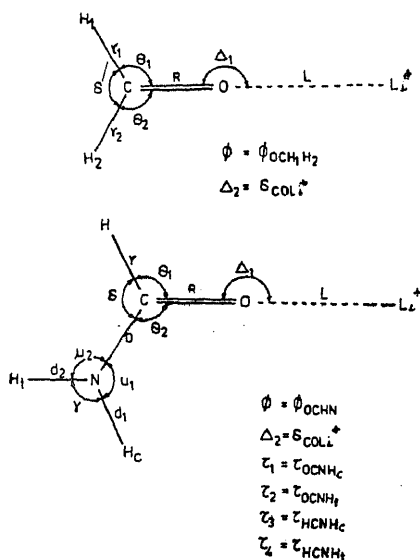
Cis and trans with respect to C = O bond

* Distances in Å, Angles in degrees and Energies in kcal mole⁻¹

† Reference for formaldehyde complex : Schuster *et al* (1975b)
and for formamide complex : Rode *et al* (1974)

° Constrained values

has arrived at an LiOC angle of 60° for complexes of Li^+ with H_2CO and HCONH_2 , the complex being planar in the case of formaldehyde donor and the lithium ion placed perpendicular to the molecular plane in the case of formamide donor. Such strange geometries have been proved to be an artefact of the CNDO method (Schuster *et al* 1975a; Rode 1974). In contrast, *ab initio* calculations have invariably resulted in a linear COLi^+ arrangement (Schuster *et al* 1975a). Recent thorough x-ray crystallographic investigations (Chakrabarti *et al* 1981) on N-methylacetamide complexes of Li, Na, K, Mg and Ca have shown that metal ions deviate from the direction of the lone pair of the carbonyl oxygen. Deviation from the lone pair direction is generally found in other oxygen donor complexes of alkali and alkaline earth metal cations (Poonia and Bajaj 1979). In the present study however, the geometry optimization was restricted to a linear COLi^+ arrangement. The CNDO/F optimized geometries of the complexes of lithium cation with formaldehyde and formamide are compared with the CNDO/F optimized geometries of the donor systems (Murthy and Ranganathan 1982d and e) in table 1. The $\text{O}-\text{Li}^+$ distances and the interaction energies of the complexes have been compared with *ab initio* results (Schuster *et al* 1975b; Rode and Preuss 1974). The geometry of the $\text{Li}^+-\text{HCONH}_2$ complex has also been calculated by Corongiu *et al* (1980) using *ab initio* wavefunctions and is not very different from that reported by Rode and Preuss (1974). The changes observed in the $\text{C}=\text{O}$ and $\text{C}-\text{N}$ bond lengths are consistent with chemical facts. The greater energy of interaction for the formamide complex over the formaldehyde complex is in agreement with the *ab initio* results of Del Bene (1979). The CNDO/F optimized geometries have been used to calculate the G matrix elements, based on the redundancy-free internal coordinates listed in table 2. Figure 1 illustrates the internal coordinates of the complexes under investigation.



Coordinate	Description
$\text{Li}^+-\text{H}_2\text{CO}$:	
In-plane :	
1. $R_1 = \Delta R$	CO stretch
2. $R_2 = \Delta L$	OLi ⁺ stretch
3. $R_3 = \Delta r_1$	CH stretch
4. $R_4 = \Delta r_2$	CH stretch
5. $R_5 = 6^{1/2} (2\Delta\delta - \Delta\theta_1 - \Delta\theta_2)$	HCH deform
6. $R_6 = 2^{-1/2} (\Delta\theta_1 - \Delta\theta_2)$	CO rock
7. $R_7 = \Delta (\Delta_1)$	COLi ⁺ bend
Out-of-plane :	
1. $R_8 = \Delta\phi$	CO wag
2. $R_9 = \Delta (\Delta_2)$	COLi ⁺ bend
$\text{Li}^+-\text{HCONH}_2$:	
In-plane :	
1. $R_1 = \Delta R$	CO stretch
2. $R_2 = \Delta L$	OLi ⁺ stretch
3. $R_3 = \Delta r$	CH stretch
4. $R_4 = \Delta D$	CN stretch
5. $R_5 = 2^{-1/2} (\Delta d_1 + \Delta d_2)$	NH ₂ stretch
6. $R_6 = 2^{-1/2} (\Delta d_1 - \Delta d_2)$	NH ₂ stretch
7. $R_7 = 6^{-1/2} (2\Delta\delta - \Delta\theta_1 - \Delta\theta_2)$	NCH deform
8. $R_8 = 2^{-1/2} (\Delta\theta_1 - \Delta\theta_2)$	CO rock
9. $R_9 = 6^{-1/2} (2\Delta\gamma - \Delta\mu_1 - \Delta\mu_2)$	NH ₂ deform
10. $R_{10} = 2^{-1/2} (\Delta\mu_1 - \Delta\mu_2)$	NH ₂ wag
11. $R_{11} = \Delta (\Delta_\theta)$	COLi ⁺ bend
Out-of-plane :	
1. $R_{12} = \Delta\phi$	CO wag
2. $R_{13} = \Delta (\Delta_2)$	COLi ⁺ bend
3. $R_{14} = 2^{-1} (\Delta\tau_1 + \Delta\tau_2 + \Delta\tau_3 + \Delta\tau_4)$	NH ₂ torsion
4. $R_{15} = 2^{-1} (\Delta\tau_1 - \Delta\tau_2 + \Delta\tau_3 - \Delta\tau_4)$	NH ₂ wag

The CNDO/F force constants evaluated for the $\text{Li}^+-\text{H}_2\text{CO}$ and $\text{Li}^+-\text{HCONH}_2$ systems are presented in tables 3 and 4 respectively. It is noticed that the CNDO/F estimates of the diagonal stretching force constants of $\text{Li}^+-\text{H}_2\text{CO}$ (cf. table 3) differ considerably from those of H_2CO (Murthy and Ranganathan 1982d). For example, the C = O stretching force constant has been calculated to be 32.687 mdyneÅ⁻¹ for $\text{Li}^+-\text{H}_2\text{CO}$ and 34.214 mdyne Å⁻¹ for H_2CO . This is expected,

Table 3. Redundancy-free internal compliance constants for lithium cation formaldehyde complex.

Force constant†	Calc. (*) CNDO/F	Calc. for H ₂ CO	Final values	Compliance constant†	Calc. (*)
F _{1,1}	32.687	12.881	12.305	C _{1,1}	0.087
F _{1,2}	— 0.905	...	— 0.453	C _{1,2}	0.066
F _{1,3}	0.539	0.469	0.469	C _{1,3}	— 0.009
F _{1,5}	— 0.504	— 0.427	— 0.427	C _{1,5}	0.067
F _{2,2}	1.170	...	0.585	C _{2,2}	1.761
F _{2,3}	0.027	...	0.014	C _{2,3}	— 0.012
F _{2,5}	0.024	...	0.024	C _{2,5}	0.023
F _{3,3}	11.854	4.334	4.369	C _{3,3}	0.234
F _{3,4}	0.142	0.142	0.142	C _{3,4}	— 0.009
F _{3,5}	0.636	0.020	0.020	C _{3,5}	— 0.016
F _{3,6}	— 0.107	— 0.142	— 0.142	C _{3,6}	0.040
F _{3,7}	— 0.047	...	— 0.047	C _{3,7}	0.114
F _{5,5}	0.631	0.541	0.541	C _{5,5}	1.902
F _{6,6}	0.841	0.856	0.856	C _{6,6}	1.181
F _{6,7}	0.005	...	0.005	C _{6,7}	— 0.025
F _{7,7}	0.098	...	0.098	C _{7,7}	10.327
F _{8,8}	0.491	0.399	0.399	C _{8,8}	2.567
F _{8,9}	0.043	...	0.043	C _{8,9}	— 0.563
F _{9,9}	0.197	...	0.197	C _{9,9}	5.197

* This work

†Units for force constants: stretch-stretch in mdyn A⁻¹; stretch-bend in mdyn rad⁻¹ Bend-Bend in mdyn a rad⁻²; and Compliance constants: stretch-stretch in a mdyn⁻¹ stretch-bend in rad mdyn⁻¹; Bend-Bend in rad² A⁻¹ mdyn⁻¹.

from the change in the C = O bond length (cf. table 1). Sadlej (1980), however has calculated these force constants to be 14.50 mdyn A⁻¹ for H₂CO and 16.15 mdyn A⁻¹ for the Li⁺ c mplex. An initial calculation after scaling the stretching force constants and the stretch-stretch interaction constants by 0.5 (Murthy and Ranganathan 1982 a and b), yielded good estimates of the Li⁺-O stretching frequency (around 400 cm⁻¹) which is in good agreement with the experimental value for the lithium ion—acetone system (Wong *et al* 1971). However, other frequencies were not reliable enough for determining frequency shifts of the donor molecule upon complexation. This is because the CNDO/F force constants require considerable refinement with experimental frequencies before the frequency shifts can be evaluated. Unfortunately, experimental frequency data is not available for 1:1 metal-ligand complexes. Under the circumstances, a viable

Table 4. Compliance-free internal compliance constants for lithium cation formamide complex.

Force constant†	Calc. (%) CNDO/F	Calc. for HCONH ₂	Final values	Compliance constants‡	Calc. (%)
F _{1,1}	30.380	12.301	12.121	C _{1,1}	0.09
F _{1,2}	0.406	...	0.203	C _{1,2}	— 0.020
F _{1,3}	0.598	0.478	0.478	C _{1,3}	— 0.006
F _{1,4}	2.631	2.109	2.109	C _{1,4}	— 0.020
F _{1,7}	— 0.081	— 0.604	— 0.604	C _{1,7}	0.069
F _{1,8}	— 0.484	— 0.074	— 0.074	C _{1,8}	— 0.024
F _{1,11}	— 0.029	...	— 0.029	C _{1,11}	0.059
F _{2,2}	1.248	...	0.642	C _{2,2}	1.582
F _{2,4}	0.188	...	0.094	C _{2,4}	— 0.011
F _{2,7}	0.014	...	0.014	C _{2,7}	— 0.059
F _{2,8}	— 0.023	...	— 0.023	C _{2,8}	0.064
F _{2,11}	— 0.014	...	— 0.014	C _{2,11}	0.499
F _{3,3}	11.662	4.575	4.591	C _{3,3}	0.220
F _{3,4}	0.465	0.441	0.441	C _{3,4}	— 0.012
F _{3,7}	0.102	0.010	0.010	C _{3,7}	0.001
F _{3,8}	0.213	0.071	0.071	C _{3,8}	— 0.027
F _{3,10}	0.072	0.026	0.026	C _{3,10}	— 0.007
F _{4,4}	20.076	7.680	7.766	C _{4,4}	0.143
F _{4,5}	0.531	0.456	0.456	C _{4,5}	— 0.010
F _{4,6}	0.038	0.036	0.036	C _{4,6}	— 0.001
F _{4,8}	— 0.589	— 0.308	— 0.308	C _{4,8}	0.071
F _{4,9}	— 0.320	— 0.278	— 0.278	C _{4,9}	0.087
F _{4,10}	— 0.077	— 0.069	— 0.069	C _{4,10}	0.008
F _{4,11}	0.014	...	0.014	C _{4,11}	— 0.065
F _{5,5}	14.963	6.738	6.725	C _{5,5}	0.149
F _{5,9}	0.167	0.004	0.004	C _{5,9}	— 0.007
F _{6,6}	14.260	6.676	6.635	C _{6,6}	0.151
F _{6,7}	0.075	0.010	0.010	C _{6,7}	— 0.001
F _{6,8}	0.042	0.008	0.008	C _{6,8}	— 0.002
F _{6,10}	0.196	0.020	0.020	C _{6,10}	0.006
F _{7,7}	0.826	0.882	0.882	C _{7,7}	1.299
F _{7,8}	0.153	0.235	0.235	C _{7,8}	— 0.437
F _{7,9}	— 0.019	— 0.010	— 0.010	C _{7,9}	0.007
F _{7,10}	0.068	0.037	0.037	C _{7,10}	— 0.011
F _{8,8}	0.884	0.712	0.712	C _{8,8}	1.618
F _{8,10}	0.023	0.103	0.103	C _{8,10}	— 0.259
F _{9,9}	0.532	0.454	0.454	C _{9,9}	2.258
F _{10,10}	0.544	0.558	0.558	C _{10,10}	1.840
F _{11,11}	0.044	...	0.044	C _{11,11}	23.052
F _{12,12}	0.618	0.549	0.549	C _{12,12}	1.822
F _{13,13}	0.054	...	0.054	C _{13,13}	18.692
F _{14,14}	0.038	0.015	0.015	C _{14,14}	65.041
F _{15,15}	0.077	0.066	0.066	C _{15,15}	15.136

Table 5. Calculated frequencies (in cm^{-1}) for lithium cation formaldehyde complex.

Species	H_2CO^*	$\text{Li}^+-\text{H}_2\text{CO}$	Approximate Description
A_1	2796.9	2802.4	CH stretch
	1750.4	1738.2	CO stretch
	1510.5	1514.4	HCH deform
	...	402.0	OLi^+ stretch
B_2	2855.7	2858.0	CH stretch
	1257.7	1260.4	CO rock
	...	169.0	COLi^+ bend
B_1	1168.2	1179.4	CO wag
	...	245.1	COLi^+ bend

* H_2CO gas phase frequencies from Murthy and Ranganathan (1982d)Table 6. Calculated frequencies (in cm^{-1}) for lithium cation-formamide complex

Species	HCONH_2^*	$\text{Li}^+-\text{HCONH}_2$	Approximate Description
A'	3533	3514	NH_2 stretch
	3413	3427	NH_2 stretch
	2880	2883	CH stretch
	1713	1686	CO stretch
	1594	1535	NH_2 deform
	1402	1422	HCN deform
	1286	1301	CN stretch
	1091	1076	NH_2 rock
	563	552	CO rock
	...	421	OLi^+ stretch
	...	88	COLi^+ bend
A''	1046	1091	CO wag
	602	592	NH_2 wag
	289	282	NH_2 torsion
	...	119	COLi^+ bend

* HCONH_2 solution phase frequencies from Murthy and Ranganathan (1982e)

viz. $\text{O}-\text{Li}^+$ stretching and in-plane and out-of-plane COLi^+ bending modes as evaluated by the CNDO/F method were introduced into the refined force constant matrix (obtained by the inversion of the refined compliance constant matrix of the donor). Since there is significant variation in the diagonal stretching force

example, the factor is 32.687/34.214 for the C = O stretching mode in $\text{Li}^+ - \text{H}_2\text{CO}$ complex. The resulting force constants are shown in column 4 of table 3.

A similar approach has been adopted in the case of $\text{Li}^+ - \text{HCONH}_2$. These force constants have been used to construct the compliance constant matrices, which in turn, have been used to calculate the frequencies of vibration for the complexes of Li^+ with H_2CO and HCONH_2 . These frequencies have been compared with the fundamentals of the donor systems (as calculated by Murthy and Ranganathan 1982d and e) in tables 5 and 6 respectively. Approximate descriptions of the vibrational frequencies of the complexes are also given in these tables, based on their potential energy distributions. Any comparison of the frequencies calculated in this study with those of Bukowska and Miaskiewicz (1981) is not valid because of the differences in experimental conditions.

In the $\text{Li}^+ - \text{H}_2\text{CO}$ complex, the C = O stretching frequency shifts to a value lower by 12 cm^{-1} . The observed C = O shift for the Li^+ complex with acetone is only about -4 cm^{-1} (Gulik-Krzywicki and Kecki 1965). It is interesting that the asymmetric and symmetric C—H stretching frequencies shift to higher values on complexation. The O— Li^+ stretching frequency is calculated to be 402 cm^{-1} , and this value is in excellent agreement with the range of experimental frequencies obtained with several donors (Rao 1973). The calculated COLi^+ linear bending modes at 169 cm^{-1} (in-plane) and 245 cm^{-1} (out-of-plane) have still not been experimentally identified.

For the formamide complex, the C = O stretching frequency shift is more pronounced and calculated to be -27 cm^{-1} . The N—H, C—H and C—N stretching modes are all shifted to higher frequencies. The predicted shift of the C—H stretching vibration to higher frequencies is in agreement with the experimental observation of Bukowska and Miaskiewicz (1981). The O— Li^+ stretching frequency has a value of 421 cm^{-1} which is in agreement with the value predicted by Rao (1973). The COLi^+ linear bending modes are estimated to occur at 88 cm^{-1} (in-plane) and 119 cm^{-1} (out-of-plane).

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